TEXTILE RESEARCH

Publication of

United States Institute for Textile Research, Inc.

CHARLES H. CLARK, *Managing Editor,*

Publication Office: Prince and Lemon Sts., Lancaster, Pa.

Editorial and General Offices: 65 Franklin St., Boston, Mass.

Board of Editors

DR. W. E. EMLEY

PROF. L. A. OLNEY

PROF. E. R. SCHWARZ, *Chairman*

Publication Committee

WILLIAM W. BUFFUM

ERNEST N. HOOD

CHARLES H. CLARK, *Chairman*

Vol. IV **September, 1934** **No. 11**

CONTENTS

The Editor's Page 490

The Micellar Arrangement in Various Cellulose Fibres. D. R. Morey 491

The Thermodynamics of Swelling. R. L. Steinberger.... 531

A Suggested Standardization of Breaking Strength Tests for Rayon Yarns. Irving J. Saxl 525

Abstracts 533

Book Review 540

Entered as second-class matter, November 17, 1932, at the Post Office at Lancaster, Pa., under the Act of Congress of March 3, 1879.

Copyright, 1934, United States Institute for Textile Research, Inc. Made in United States of America.

Issued monthly at Prince and Lemon Streets, Lancaster, Pa., for United States Institute for Textile Research, Inc., Boston, Mass.

Subscription price $5.00 a year. Single copies .50.

The Editor's Page

SEVERAL of our readers have been frank enough to confess their limited knowledge of the use of the X-ray and of fluorescence for polarization, as now commonly utilized in fibre analysis, and have asked to be referred to sources of relatively simple expositions of these subjects. Your managing editor confesses that he has experienced an identical failing and need. His search of the literature of these subjects causes him to recommend the following books as being reliable, interesting and among the least abstruse:

For polarized light and its application, Chapters 13 and 14 of "Textiles and the Microscope," by Prof. E. R. Schwarz. McGraw-Hill Book Co., New York, N. Y.

For X-ray diffraction photographs and their interpretation, Chapters 3 and 4 of "Fundamentals of Fibre Structure," by W. T. Astbury. Oxford University Press, New York, N. Y.

Conference Subjects

THE conferences held last Spring by U. S. Institute on Fabric Wear and Wear Testing, and on the Sizing of Cotton and Rayon Warps, were resultful in defining the character of scientific research that is needed to solve certain, at least, of the problems involved. They also demonstrated that such meetings of interested groups and authorities may play an important function in interpreting completed scientific research to the practical men of the industry.

Because of these results, and of the large attendance at these gatherings, U. S. Institute's research committee is desirous of receiving from members of U. S. Institute suggestions of subjects for additional conferences. It may be stated, however, that many members have expressed the hope that another conference on sizing may be held in the Fall that will include worsted warps and also finished goods, and this suggestion will receive consideration at the next meeting of the committee.

Kindly forward your suggestions to the Secretary of U. S. Institute.

The Micellar Arrangement in Various Cellulose Fibres

By D. R. MOREY *

Summary

The fluorescence from fibres dyed with strongly fluorescent direct dyes is examined for polarization, and the result interpreted in terms of the micellar orientation and spiral structure of the fibres. Results on a number of natural and artificial cellulose fibres are given and discussed.

Introduction

THE results presented in this report were obtained using the fluorescence method which has already been described in this journal.[1] However, a brief review at this point will provide a helpful introduction to the pages which follow.

The fibre is dyed with a strongly fluorescent dye and is rendered visible in a microscope by the fluorescence excited by ultra-violet radiation from a mercury arc. The exciting ultra-violet radiation is not polarized, but in general the fluorescence is partly polarized. The microscope is equipped to make quantitative measurements of the percent. of polarization, for it is this polarization phenomenon which reveals the micellar arrangement.

The method is founded upon the ability of certain dye molecules to assume and/or imitate the arrangement in space of the molecular or micellar groups to which they are attached. In the case of cellulose, the direct dyes possess this ability. The degree and direction of alignment of a number of fluorescing molecules is directly obtained from the percentage polarization of the light emitted from those molecules. As extreme cases, we have completely random arrangements resulting in non-polarized light; and perfect parallelism of each dye molecule to every

* Dr. Morey is a senior fellow of the Textile Foundation working under the direction of Prof. Ernest Merritt, Dept. of Physics, Cornell University, Ithaca, N. Y.

other, resulting in 100% plane polarized light. If, then, the dye molecules attach themselves to the underlying structure in a definite single-valued manner, we have at once a means of studying the structure. On the other hand, if the structural features are known, and we apply different dyes, we have a means of getting at the manner of dye deposition.

The manner of attachment of dye molecule to micelle, which must exist if measurements of polarization are indicative of the fibre structure itself, is illustrated by the ordinary electric light bulb and its socket. The bulb may be attached to the socket only in a definite manner which preserves, for any position of the socket, the same relative arrangement of the two parts. We may deduce the spatial arrangement of a number of sockets in a room, even though they are not directly visible, by looking at the luminous bulbs. By dyeing the fibres we figuratively attach to the micelles little light bulbs which indicate the micellar positions. A union between micelle and dye molecule, which could occur with different relative positions of the two, would not permit the application of this method.

There are, however, a number of indications that, for certain dyes, the attachment is directionally single-valued. Those indications dealing with anistropic forces of the Van der Waals' type resulting in dichroic phenomena have already been discussed.[1] A simple experiment illustrating them may be performed by growing potassium nitrate crystals from a solution containing a very small amount of Thioflavine S or Primuline. Such crystals exhibit polarized fluorescence.

Method of Measurement

The most convincing justification for the basic assumptions underlying the polarized fluorescence method is the essential agreement of the results obtained by its use with the well established knowledge of orientation and spiral structure built up by X-ray and optical methods.

Fig. 1 illustrates the type of result obtained. The angular position of the analyzing prism, which is mounted behind the microscope objective and which rotates about the microscope axis, is plotted along the horizontal axis of the graph. The fibre is always set so that its axis is parallel to the electric vector direction of the analyzer when the analyzer reading is zero. Thus the angular position of the prism, read on the scale plotted along the horizontal axis, gives the angle between fibre axis and direction of the electric vector of the light transmitted through the prism to the eye. The intensity of the transmitted fluorescent light (measured by a

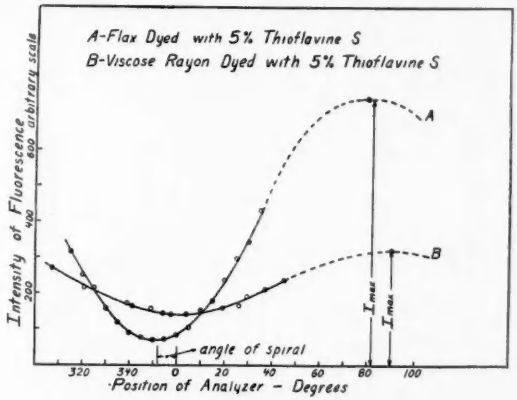
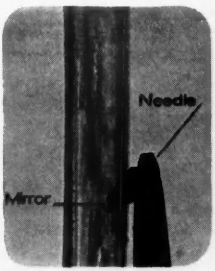


FIG. 1.

comparison source of light which illuminates a small mirror in the eye-piece, see Figs. 2, 3 and 4) is plotted as ordinate. Curve A (Fig. 1) was obtained with a flax fibre, curve B with a viscose rayon filament. From studies with white light and a polarizing microscope it is known that flax is a better oriented material than viscose. These curves give us an opportunity to quantitatively compare the two fibres. The percent. orientation is obtained by placing the maximum and minimum intensity values of the curve in the formula

$$\% \text{ orientation} = \frac{I_{max} - I_{min}}{I_{max} + 2\ I_{min}} \times 100$$



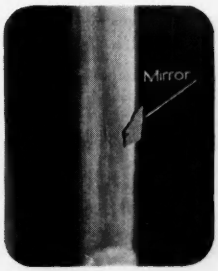


FIG. 2. FIG. 3. FIG. 4.

FIG. 2. Flax fibre; visible transmitted light.
FIG. 3. Flax fibre; analyzer transmitting fluorescence.
FIG. 4. Flax fibre; analyzer extinguishing fluorescence.

We thus obtain for the orientation of the flax fibre 77% and for the rayon filament 31%.

The spiral arrangement of the fibre is also directly obtainable from the curve. It will be proven later that the device measures the average spiral; it is sufficient to state here that this spiral value is given by the number of degrees between the analyzer zero and the minimum point of the curve. Looking at curve A (Fig. 1), we see that the spiral at this point of the flax fibre is 8°. As we should expect, no spiral structure is indicated by curve B, viscose rayon, since its minimum point comes at 0°.

Fig. 2 shows a flax fibre in transmitted visible light. The comparison field for intensity measurement of the fluorescence is the small piece of mirror-backing seen on the end of the needle. The appearance of the same fibre fluorescing, with the analyzer at 352° (corresponding to the curve maximum) is shown in Fig. 3. Fig. 4 shows the appearance with the prism turned 90° so that the intensity is a minimum. The great change of intensity of the fibre can be realized by noting the comparison field, the adjustment of which has not been changed.

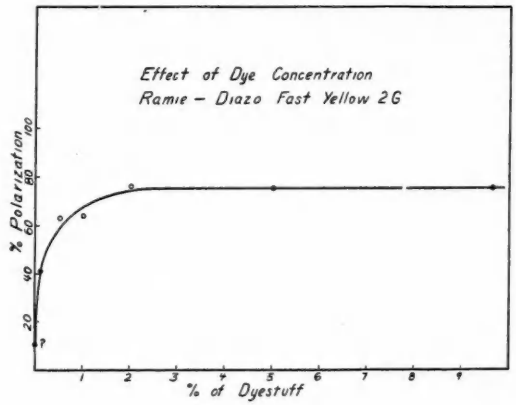


FIG. 5.

Effect of Dye Concentration

Before we can place full confidence in such results, we must answer this question: Does the degree of success attained by the dye molecules in assuming the orientation of the micelles vary with the dye concentration, and, if so, what is the best concentration to use? This has been answered experimentally by dyeing similar fibres with various dye concentrations. In Fig. 5 are the results of dyeing a number of ramie samples with Diazo Fast Yellow 2G (General Dyestuff Corp.) with the concentrations of dye in the bath ranging from 0 to 10% of the fibre weight. (For details of the dyeing procedure see appendix.) With 0% there is only the cellulose fluorescence, which is quite weak and poorly polarized. The low intensity

renders measurement difficult. As the dye molecules are placed on the fibre and add their fluorescence, the poorly polarized cellulose fluorescence becomes a smaller and smaller fraction of the whole, until at 2% it is negligible. The flatness of the curve from this point on is a very desirable feature. It means that one does not have to be particular about the concentration. A similar experiment was performed by mounting a flax fibre in a brass holder which could be immersed in the dye bath, thus increasing dyeings, and the observations could be made on the same portion of the same fibre. This time Thioflavine S (DuPont) was used. The actual curves obtained are shown in Fig. 6 and the orientation-dye con-

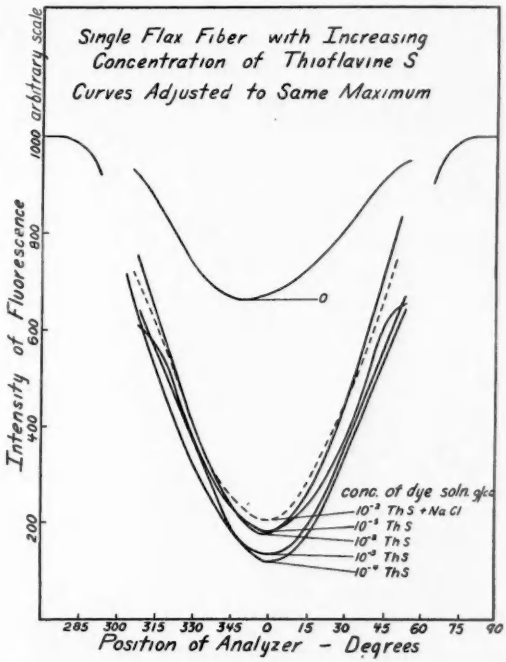


FIG. 6.

centration relation is shown in Fig. 7. It is similar to Fig. 5, with the additional information that at very high concentrations the orientation falls off again. Evidently, at the high concentrations, the dye aggregates are beginning to crowd and disturb one another in their efforts to cling to the micelles; while at the lower concentrations they are far enough apart not to influence each other. However, the range over which the micellar orientation is faithfully reproduced is quite astonishing. A simple general rule

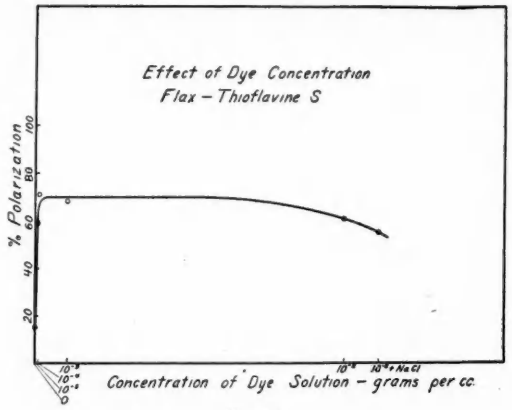


FIG. 7.

is to dye the fibre with a dye and with a concentration which results in good fluorescence. Weakly fluorescing dyes result in a lowered percent. polarization, because the relatively unpolarized cellulose fluorescence begins to play a part. In such cases the percent. of polarization cannot be interpreted as micellar orientation, so they should be avoided. Good examples of these cases are the results obtained with Primuline and Diazo Fast Yellow 2G before and after diazotization and development with beta naphthol. In the undeveloped state both dyes fluoresce well and on ramie show a polarization of about 70%. After development, the fluorescence, especially that of Primuline, is considerably less intense. The polarization of developed Diazo Fast Yellow 2G was found to be 42%, and that of developed Primuline 20%. Some of the direct dyes, and all of the tannin mordant dyes so far used, fluoresce weakly and give low values. Humidity does not affect the results and requires no control.

Results on Various Fibres

The following results were obtained using chiefly a 5% dyeing with Thioflavine S (DuPont) although Diazo Fast Yellow 2G (Gen. Dye. Corp.) and Primuline (DuPont) were also used. All three yielded similar results. Since a fair amount of work is required to obtain a curve such as is shown in Fig. 1, the number of curves which can be taken is limited. Therefore the fibre portion on which the quantitative run is made is selected by rapid qualitative observations of the entire fibre, or several fibres, as a good representative spot. Places showing peculiarities or distortions are not chosen. For example, the joints or transverse markings of flax and ramie can hardly be said to have a micellar arrangement representative of those fibres. To include the joints in a statement of the fibre orientation one can state the relative volume of the fibre which they occupy thus: flax shows an orientation of some 73% with 5–10% of unoriented structure.

Flax

This is the most highly oriented of the fibres so far examined. An average of the results of 15 curves gave 73%. The highest value observed was 85%, although small fibrils, sometimes seen torn from the fibre, seemed to have even greater values, running up to perhaps 90%.* However, due to their minuteness, no measurements could be made; hence this figure is a guess. The average deviation from the mean of 73% was $\pm$ 7%. This $\pm$ 7% is a measure of the natural structural variation from fibre to fibre; it is not an expression of the accuracy of measurement. Each individual curve yields a value accurate to plus or minus one or two per-cent. This is discussed in detail in the appendix.

That the orientation exceeds that of ramie (69%) is at first surprising, considering the popular belief to the contrary, and the great use made of ramie for X-ray diffraction patterns. However, flax shows a distinctly greater spiral than ramie, having a mean value of 5½°, with an average deviation from the mean of $\pm$ 3°. This greater spiral means a spreading of each X-ray spot into an arc larger than would be the case with ramie, and a photograph indicative of lesser orientation results. If the spiral angle is of the order of 10° or greater, two spots appear instead of the single one obtained with a parallel structure. With the small spirals these two spots merge and cannot be recognized as such.

As with the orientation, the $\pm$ 3° deviation from the mean is a real measure of the spread or variation of the spiral itself, for each spiral value is accurate to some $\pm$ ½° as will be shown later.

Ramie

Twenty-six determinations on ramie resulted in a mean orientation of 69%, with an average deviation from the mean of $\pm$ 6%. The spiral, which runs in the same direction as that of flax, had a mean value of 3½° with an average deviation from the mean of $\pm$ 1°. Ramie thus shows much less variation in spiral than flax, which is another reason why it yields sharp diffraction patterns despite its slightly lower orientation.

The many joints or markings which characterize ramie show no orientation, indicating a randomly distorted structure.

Hemp

The mean orientation of hemp, as determined from 14 curves, was 59%, with an average deviation from the mean of $\pm$ 7%. Hemp is of particular interest because it shows no spiral. The average spiral was 0°, with an average deviation from the mean of $\pm$ ½°. In both Kentucky and Italian hemp, cross markings were observed which were inclined to the diameter at a 10° angle. Since a spiral structure was lacking, it would appear that one cannot always accurately obtain the spiral angle on the

* The percent. polarization values for very well oriented structures are probably somewhat lower than the true orientation, for the small amount of poorly polarized cellulose fluorescence is perhaps appreciable when the dye fluorescence is almost completely extinguished. Thus the minimum point is raised, and the percent. polarization lowered.

assumption that such fissures run perpendicular to the spiralling fibrils. An X-ray diffraction photograph showed no spiral, although one of 10° could have been detected. Fig. 8 shows a portion of a hemp fibre, the photograph being taken with the ultra-violet-excited fluorescence. The dye has gone into the cross markings in an unoriented manner. Fig. 9 is the same portion taken with visible, transmitted light. The conditions of illumination are quite different in the two cases. In Fig. 8 we are dealing with a self-luminous body in which the usual interference between closely adjacent points is impossible, for each point is independently illuminated. This has the effect of increasing the numerical aperture of the microscope lens system.

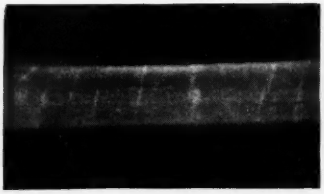


FIG. 8.

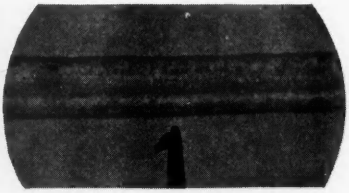


FIG. 9.

FIG. 8. Fluorescing hemp fibre, showing cross marks.
FIG. 9. Hemp fibre of Fig. 8 in visible transmitted light.

The pronounced difference in the value of the spiral angles for flax and hemp provides a direct and positive means for differentiating the two fibres. While many of the textile fibres have outstanding characteristics which make their identification easy, flax and hemp fibres have so many features in common that in a finished article it is difficult to distinguish them. A. Herzog [2] gives several means of distinguishing flax from hemp. Among them are four tests, different superficially, but all manifestations of one fundamental difference—that of the degree of spiral. The first is to clamp one end of the fibre, place a small paper marker on the other, and wet the fibre. It will then turn about, if flax, for several turns to the left. If hemp, it will act undecided, with perhaps a greater movement toward the right, but in all cases with a much smaller amount of turning than flax.

The next test consists of treating the fibres with dilute cuprammonium solution and examining with the microscope. The fibril structure is then seen, and with flax the striations are well defined and run on the wall-side toward the observer from lower right to upper left. The swelling is rather uniform. Hemp behaves much like cotton, swelling in irregular masses, constricted here and there by remains of a middle lamella. The hemp wall may show striations, but they are not well defined, and run in an irregular manner in the swollen sample.

The third and fourth points deal with the interference colors between crossed nicols, without and with swelling of the fibre. Herzog says: "Many flax and hemp fibres show very weak or no brightness in the orthogonal position; this is especially true for hemp. . . . I attempted to use strong

swelling agents in those cases where a fibre showed no brightening, to intensify the optical action. Only with flax were successful results obtained. It was striking that flax in both orthogonal positions lighted up more brilliantly than before swelling. Most probably this occurrence is in direct connection with the less steep position of the spiral stripes in the cell wall (caused by the strong contraction of the fibre.) For hemp this was much less clearly seen.''

It is evident that all these points of differentiation are manifestations of one fundamental difference, namely a difference in the angle of spiral. Because several phenomena have their origin in the angle of spiral, it might well be termed a basic or fundamental property. The other quantity obtained from these experiments, the percentage orientation, is also a basic property. The role of orientation in tensile strength, elastic properties, dyeing, and its correlation with the differences in refractive index, dielectric constant and magnetic permeability measured parallel and perpendicular to the fibre axis have been pointed out in other papers, and need no discussion here. While speaking of fibre differentiation, however, it is of interest to point out that identification by means of the interference colors obtained in an ordinary polarizing microscope is a measurement based on the degree of orientation possessed by the fibre.

Sisal

Sisal is of interest as an example of a structure with a large spiral. The mean of eight curves was 30°, with the spiral direction opposite to that found in flax and ramie. The average deviation from the mean was $\pm 6°$. While looking over some fibres with the fluorescent illumination and a magnification of 950, one was observed in which a detailed fibril structure was visible. Those fibrils projecting from the edge were easily seen; those in the center were detected by changing focus slightly. In other fibres such a considerable amount of fibril structure was not found; this particular fibre had at some time suffered some abrasion which happened to make the fibrils stand out. They were estimated as being less than .3 mμ in diameter. A direct measure of the average angle which these fibrils made with the fibre axis, using a cross-hair and the rotating stage, gave a value of 25°. This same spot was also analyzed in the usual manner and the resulting curve is shown in Fig. 10. The agreement of the directly determined 25° value with the positions at which the two minima and the maximum occur (24°, 24°, 26°), speaks for itself.

The mean orientation of single fibres was 22% and the average deviation from the mean was $\pm 4\%$. There are indications that for large spirals the percent. polarization is lower than the true orientation, so the value of 22% is probably low by several percent. When bundles of fibres are examined the percent. polarization is always lower than that obtained on a single fibre, as we might expect from a juxtaposition of joints, good portions, intercellular matter, etc. Sisal bundles show nearly zero polarization, while bundles of the better oriented fibres, although not near zero, are appreciably below the values for single fibres.

Cotton

From the discussion of the previous cases we have a view of how orientation and spiral may vary within limits on one kind of fibre, and how each

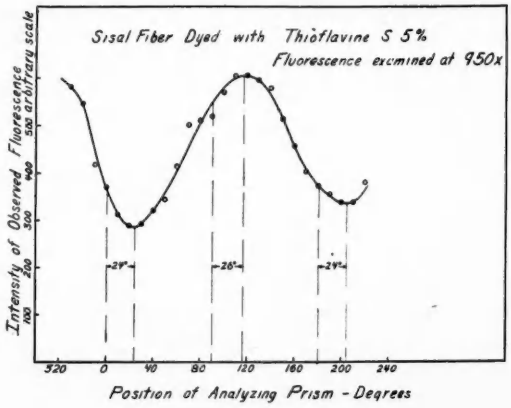


FIG. 10.

kind of fibre has mean values of orientation and spiral which are characteristic of it. When we come to cotton, we find that its distinguishing characteristic seems to be the absence of a well defined value of orientation or spiral. Cotton is marked by its extreme variation in these properties. Besides the usual qualitative observations on numbers of fibres, 35 accurate orientation and spiral measurements were made on a sample of American (S.C.) cotton. The mean orientation was 39%, with an average deviation from the mean of $\pm$ 15%. These figures are also representative of an independent South Carolina sample and a Kentucky sample. Even over a small area of a single fibre the orientation was sometimes found variable.

Fig. 11, taken with incident visible light, shows a portion of a cotton fibre placed close to the comparison mirror and ready for intensity read-

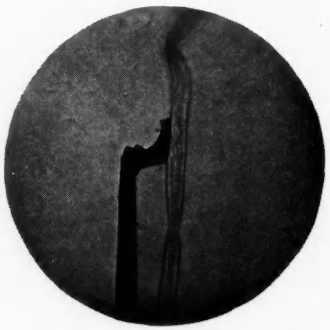


FIG. 11. Cotton fibre; visible transmitted light.

ings. Fig. 12 shows the same portion, this time being illuminated by ultra-violet radiation, and the photograph taken by fluorescent light. The analyzer has been set so that the part of the fibre near the mirror is at its maximum intensity. Upon rotating the analyzer 90°, Fig. 13 is obtained. The same portion (near the comparison field which has been very much re-reduced in intensity) is now less intense, indicating a polarization of the fluorescence and an orientation of the fibre at that point. However, it can be seen that the edges of the lumen and some irregular lines have suffered very little loss of intensity, indicating that in those places the dye molecules are taken up in a random and irregular fashion.

Although an average orientation value can be assigned to cotton which has some meaning despite the marked variation, such does not seem to be the case with the spiral values obtained, for the value ranged from a 45° spiral in one direction to a 50° spiral in the other. Over one convolution

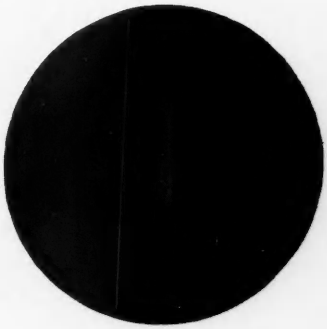


FIG. 12. Cotton fibre; analyzer transmitting fluorescence.

FIG. 13. Cotton fibre; analyzer extinguishing fluorescence.

of a certain fibre the direction of spiral was found to vary 50°, and the same variation was also found for two points separated by .05 mm. The curves for this latter case are given in Fig. 14. Curve A also shows how portions of the fibre may be quite perfectly formed; the orientation computed from this curve is 77%. This is, of course, an exceptional case. The orientation may vary on a single fibre from this high value to 15–20%. The variation of spiral direction over parts of a fibre makes itself evident when the analyzer is continuously rotated and the fibre observed. *Different parts* of the fibre are seen to darken (extinguish) at different times, unlike the case of hemp, ramie or flax, when the *whole fibre* grows dark or light at certain analyzer positions. Figs. 3 and 4 of flax, show how a uniform fibre behaves. The behavior of cotton is illustrated in Figs. 12 and 13. In Fig. 12 it can be seen that the part near the mirror is more intense than portions below, and in Fig. 13, upon rotating the analyzer, the intensities are reversed. Thus the structural directions in these neighboring portions differ by roughly 90°. There seems to be more tendency to spiral in the flax direction (lower right to upper left on the fibre side toward

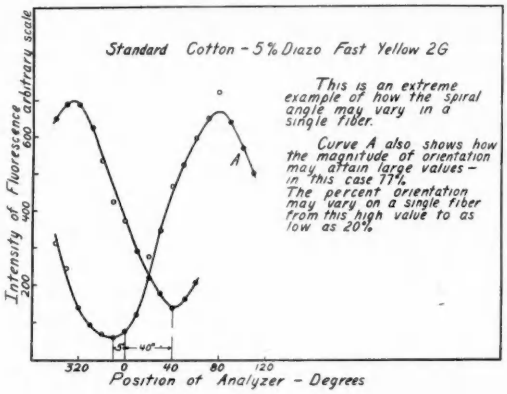

Standard Cotton - 5% Diazo Fast Yellow 2G
This is an extreme example of how the spiral angle may vary in a single fiber.
Curve A also shows how the magnitude of orientation may attain large values — in this case 77%. The percent orientation may vary on a single fiber from this high value to as low as 20%
Intensity of Fluorescence 600 arbitrary scale
200
400
A
320
0
40
80
120
Position of Analyzer - Degrees

FIG. 14.

the observer) but this may have been due to a chance distribution of the observations. The point is quite uncertain.

Of several mercerized samples, some showed a tendency toward more uniformity of the results, while others were as variable as in the cases just cited. The mode of treatment, and especially the tension applied during mercerization, play an important part.

To compare various grades of cotton, where some sort of average value of orientation is desired, the X-ray method of measurement,[3] is much to be preferred, for, by using a large number of fibres and a wide beam, an average or integrated value over a considerable volume of the fibres is at once obtained. Where the individual fibres are so variable it becomes a long and tedious process to examine optically a sufficient number to arrive at a reliable average. It is interesting to point out that the two methods, when applied to cotton, do not measure quite the same thing. The optical value is a measure of the deviation of the micellar axes from the fibril direction at a given point regardless of the spiral value at that point. A diffracted X-ray beam is spread into an arc, not only by the deviation of the micelles within a fibril, but also, since many fibres are simultaneously examined, by the varying spiral directions of the fibrils themselves.

Rayons

Since we ascribe the feminine gender to nature, we might say that in making the cotton fibre she has exercised a trait popularly associated with her sex, and changed her mind several times in the making of it. In making rayon filaments man seems to have his mind fairly well made up, to judge by the uniformity of the finished product.

A sample of viscose rayon showed an orientation of 28%, with an average deviation from the mean of only $\pm$ 3%, and a sample of cuprammonium had an orientation of 47% with an average deviation of $\pm$ 4%.

These two samples were received from Dr. Sisson, who measured their orientation by his X-ray method.[3] The values he obtained were: viscose 30%, cuprammonium 46%. The agreement of the independently obtained values is very gratifying and is proof that the methods are truly quantitative.

As is to be expected, the spiral angle for rayons is zero. At some places of the viscose filaments, the ridges or striations seen on the surface varied slightly from parallelism to the filament axis, accounting for small deviations of the polarization curve minimum from the zero of the analyzer scale.

Through the kind co-operation of Dr. A. Stuart Hunter of the DuPont Rayon Co., Buffalo, seven skeins of representative viscose yarns were received whose tensile properties had been measured. Portions of these skeins were examined in order to see what correlation existed between the measured physical properties and orientation. Where the properties were marked the correlation is evident, as shown by the following data:

Sample	Tenacity (gms./denier)		% Stretch at breaking point		% Orientation
	Dry	Wet	Dry	Wet	
Bright 100/40	1.66	0.75	22.7	24.8	36.1
Bright 100/40	3.03	1.74	13.1	15.3	58.2

However, when the differences in the physical properties were smaller such clear cut correlations were not found. There are two chief reasons for this: First, that the tensile strength depends not only upon orientation, but also upon minor factors which do not enter into the orientation measurements. Second, since the orientation varies to some extent from filament to filament, and along a single filament, and undoubtedly the same is true of the tensile properties, the average orientation obtained by examining 12 microscopic portions selected at random from a skein should not be expected to agree closely with the sort of average which is struck by a tensile test. For a precise correlation of orientation with tensile properties, it would seem that both measurements must be made on the same small filament portion.

Sample	Tenacity (gms./denier)		% Stretch at breaking point		% Orientation
	Dry	Wet	Dry	Wet	
Bright 100/100	1.67	0.73	21.8	21.7	37.1
Delustered 150/40	1.54	.76	25.5	30.4	37.8
Delustered 150/90	1.54	.71	24.6	25.2	38.5
Partially ripened 150/40	1.65	.75	21.7	18.7	35.3
Completely ripened 150/40	1.50	.63	13.6	11.1	36.0

A sample of delustered Tubize nitrate rayon (100/26) when immersed in a hot bath of Rhodamine B showed an affinity for the dye, for some of it was taken up and was not removed by subsequent washing in water. The fluorescence from the Rhodamine B was completely unpolarized, although the same material when dyed with Thioflavine S produced an alignment of the dye molecules to the extent of 24% polarization. A Tubize nitrate 100/26 sample *not* delustered would not take up the Rhodamine B at all, but was easily dyed with Thioflavine S and showed 46% polarization. Since Rhodamine B is a basic dye and has no affinity for cellulose, it appears that the material introduced to reduce the luster acts as a sort of mordant, taking up the Rhodamine B, while the Thioflavine S is attached to the cellulose micelles as usual. From the zero polarization of the Rhodamine fluorescence it appears that the delustering particles are scattered randomly in the rayon filament. A similar phenomenon of two dyes being taken up by two different components of a fibre is found with jute.

A sample of Chacelon acetate rayon (45/13) showed 14% polarization with Thioflavine S and zero with Rhodamine B. Apparently different types of forces are involved in the holding of the two dyes. In the case of Thioflavine S the forces are directed and still connected with the micellar structure and direction; while in the case of Rhodamine B the forces involved are quite symmetrical with respect to the dye molecule.

A sample of acetate sheet (Eastman Kodak, courtesy Dr. J. G. McNally) took up sufficient Thioflavine S to permit good measurements. With the direction of observation perpendicular to the plane of the sheet no orientation was found, but when the edge of the sheet was examined, 11% polarization was observed. X-ray diffraction patterns were then taken in the two directions and the same phenomenon found. The forces involved in the extrusion of the sheet through a slit, and the unsymmetrical shapes of the micelles, tend to place the long direction of the micelle in the plane of the sheet. Judging from the diffuseness of the X-ray diffraction rings, the particles in the sheet are considerably smaller than those in ordinary fibres.

There are indications that some of the dyes specially developed for acetate yarn assume only a random orientation in the fibre. The problem awaits solution as to whether this is true for all acetate dyes, or whether some possess the anisotropic adsorption properties which would enable them to imitate the underlying structure.

Kapok

Using Thioflavine S, the orientation was found to vary from fibre to fibre of kapok and over single fibres, from 0% to some 20%. The spiral angle is not large, but is also quite variable, from 0° to perhaps 20°. The characteristics may best be described as those of cotton on a miniature scale. The orientation and spiral values are not as large and the variations are correspondingly of smaller magnitude.

Jute

The average orientation of jute was 35%, and the average spiral angle was zero degrees. Just a few fibres were examined; hence the values are

to be regarded as approximate. Jute displays an ability to be dyed directly with the basic dyes because of its lignin content, which has a strong affinity for such dyes. When dyed with Rhodamine B and examined, no polarization was found, indicating that the lignin content has no directive properties with respect to the fibre.

Pita Floja

The average orientation of pita floja was 26%, with considerable variation. The spiral angle was about 2° and opposite in direction to the flax spiral.

Manguey Hemp

The average orientation of fibre bundles of manguey hemp was 13% with no spiral observed. With Rhodamine B, zero polarization was found.

The Cellulose-Dye Attachment

X-ray diffraction pictures of ramie dyed directly with strong concentrations of Thioflavine S and Diazo Fast Yellow 2G, and of ramie heavily mordanted with 100% tannic acid and 50% tartar emetic, showed no evidence of change of the original cellulose structure. (See Figs. 15, 16 and 17.) The plane spacings calculated from the mordanted ramie diffraction

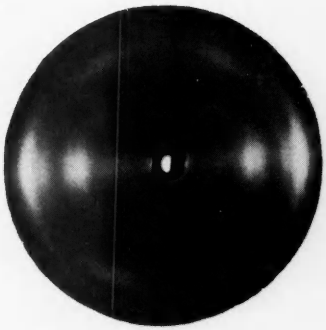


FIG. 15. Undyed ramie; Fe Kα and β radiation.

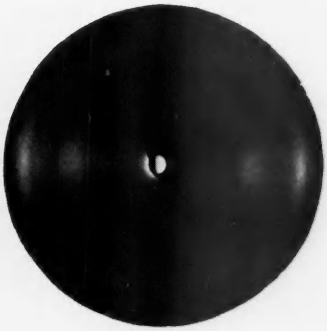


FIG. 16. Ramie dyed with 10 per cent. Diazo fast yellow 2G. Fe Kα and β.

pattern and the corresponding plane spacings of native ramie as given by Meyer and Mark[4] are tabulated on the next page.

It is therefore apparent that the dye molecules do not penetrate the well formed crystal cellulose, for if they did the lattice would surely be distorted by the foreign molecules whose diameter is much greater than the dis-

	Tannin-mordanted ramie		Unmordanted ramie (Meyer & Mark)	
	d/n	Intensity	d/n	Intensity
Equator spots	3.87	20	3.86	Very strong
	5.34	9	5.36	Fairly strong
	5.90	10	5.93	Strong
1st layer line	2.31	1	2.29	Weak
	2.60	2	2.59	Fair
	6.35	½	6.39	Weak
2nd layer line	2.84	½	?	
	3.04	½	3.07	Weak
	4.30	8	4.30	Strong
	5.12	4	5.10	Weak
3rd layer line	2.61	6	2.63	Fair
	2.92	3	2.94	Weak
	3.17	4	3.16	Weak
4th layer line	2.15	1	2.16	Weak-fair
	2.31	1	2.33	Weak
	2.57	4	2.57	Strong
On vertical axis	1.99	½	?	

tance between cellulose chains. The forces holding the chains to each other must be stronger than the forces existing between a chain (or group of chains) and a dye molecule (or group of molecules). The dye molecule must, therefore, find its way to the side of a well crystallized portion, passing through channels opened up by the solvent in the non-crystalline (and presumably less strongly bound together) portions of the fibre. Although it is quite reasonable to suppose that disorganized as well as crystalline cellulose exists in the fibre, the dye molecules are very partial to the crystalline portion, presumably because it can present stronger attractive forces. One comes to this conclusion because the fluorescence method of orientation measurement, which looks at the *dye molecules*, gives results in good agreement with the X-ray method, which observes the *crystalline portions*.

It is generally held that in direct dyeing the particles in solution are of a colloidal size, rather than molecularly dispersed. If these particles go onto the fibre without breaking up, we must suppose, in view of the high polarization obtained with a well oriented fibre, that in each colloidal particle the molecules are regularly arranged parallel to each other. Otherwise it is difficult to see how one can place on a fibre a number of particles, each with several molecules held in a number of different positions, and obtain polarized fluorescence from such a system. If we find it difficult to accept a picture of a semi-crystalline, colloidal particle, we must assume that *on the fibre* the dye is molecularly dispersed.

If we attempt to dye a fibre, say cotton, with Rhodamine B by immersion in a hot dye bath, we find that there is no attraction between the cellulose and the dye, contrary to the behavior of Thioflavine S. Rhodamine B is one of the basic dyes and requires a mordant on the fibre before it will adhere. An unmordanted fibre, immersed in a solution of Rhodamine B and allowed to dry without washing off the solution, shows little polarization of the fluorescence. The dye molecules lie nearly at random with weak directive forces holding them, for the dye is easily washed off with water.

In the course of these dye experiments a phenomenon has been observed, which has, perhaps, no close connection with the advancement of the knowledge of textiles and dyes, but is of extraordinary interest to the academic physicist engaged in the study of fluorescence. The attractive forces which hold the dye molecule to the cellulose chains are called secondary valences, Van der Waals' forces, or residual forces, in contrast to

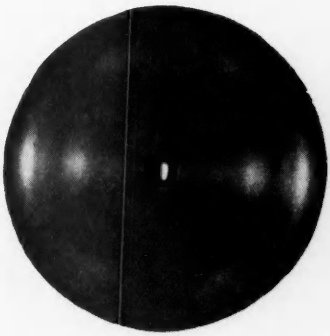


FIG. 17. Ramie dyed in a very conc. soln. of Thioflavine S. Fe Kα and β.

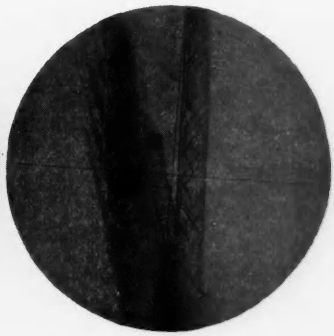


FIG. 19. Yucca fibre near end; visible transmitted light.

the primary valences of a true chemical union. These secondary attractive forces are the result of electric fields set up outside the molecule by polar groups within it.

The fluorescence is due to some kind of electronic vibration in the outer part of the molecule where the optical phenomena have their origin. Practically nothing is known about the nature of the process or of the electronic mechanism which can absorb radiant energy and emit it as fluorescence.

The experiments show a close correlation between these two mechanisms of attraction and fluorescence. Using ramie as a base material on which to study the orientation behavior of different dyes, without exception, so far, the dyes have emitted polarized fluorescence with the plane of polarization *in the same direction.* The minimum of each curve has fallen about 3° from the zero. It is reasonable to assume that in each dyeing the dyestuff met a similar structure presenting secondary forces in the same direc-

tion. The constant direction of plane of polarization thus indicates that in each case the fluorescent mechanism is located in the molecule *at a constant direction to the attractive mechanism.* Although the number of dyes examined is small, the lack of exception and the range of chemical nature point to a general rule. The following were dyed directly: Diazo Fast Yellow 2G (G.D.C.), Thioflavine S (D), Pontamine Fast Yellow NNL (D), and Primuline (D). The following were applied directly, although they do not make fast dyeings, and the orientation is very low: Safranine GFFX (Heller & Merz), Thioflavine TCN (D), Rhodamine B, and Rhodamine 6GDN (D). The following were applied on a tannin mordant: Thioflavine TCN, and Safranine GFFX. Primuline and Diazo Fast Yellow 2G were also diazotized and developed. Ramie, heavily mordanted with tannin, but not dyed, also fluoresced with the direction of polarization the same as before.

Appendix

This section contains various technical details, proofs and analyses which are necessary when presenting new results.

Estimation of Accuracy

The accuracy of the orientation measurements is determined chiefly by the ability of the observer to match the intensities of the fibre portion and the comparison mirror. In these experiments, for each setting of the analyzer at least three matchings were made. The best criterion of the accuracy is the curve itself. If the points show little deviation, and the curve is fairly symmetrical about its minimum point, the orientation should be correct to 1 or 2%. Other determiners of accuracy are to have the colors of the fibre and comparison fluorescent source closely alike; to have good prisms and to have the scale read zero when they are crossed, and to avoid a fluorescent material on the fibre or comparison source which weakens rapidly under exposure.

It is much more important to obtain the minimum intensity accurately than the maximum, as is shown by consideration of the expression

$$\% \text{ Orientation} = \frac{I_{max} - I_{min}}{I_{max} + 2\ I_{min}} \times 100$$

$$\text{For } \frac{d\ (\% \text{ Or.})}{d\ I_{min}} = -\frac{3\ I_{max}}{(I_{max} + 2\ I_{min})^2} \times 100$$

$$\text{and } \frac{d\ (\% \text{ Or.})}{d\ I_{max}} = \frac{3\ I_{min}}{(I_{max} + 2\ I_{min})^2} \times 100.$$

Thus the effect of small changes in I_{min} or I_{max} is inversely proportional to their magnitudes.

When the % orientation $= 50$, $I_{max} = 4\ I_{min}$.

When the % orientation $= 80$, I_{max} is 13 times I_{min}, and an error in the measurement of I_{min} would have 13 times the effect of the same error in I_{max}. It is therefore customary to determine the lower part of the curve fully, allowing a single point 90° from I_{min} to determine I_{max}.

To determine how closely results could be repeated, eight independent curves were obtained from the same spot on a hemp fibre. The average deviation from the mean orientation of 60.2% was $\pm$ 1.1%.

The average deviation in the measurement of the spiral angle was $\pm$ ½°.

It is highly important in determining the spiral angle to know accurately the angle between fibre axis and electric vector for a given analyzer setting. In this work a tube with a cross-hair eyepiece was designed to fit in the microscope barrel in such a position that a cross-hair was parallel to the electric vector of the light transmitted by the analyzer in its 0° position. This adjustment was made to within ¼° through use of a second prism whose electric vector direction had been accurately determined by use of the extinction positions of ammonium sulfate crystals. A fibre to be examined was placed parallel to the cross-hair, and then this eyepiece was removed and the comparison eyepiece was inserted before making the intensity readings. The correctness of the adjustments can be checked by observations on several rayons, whose curve minima should fall at zero.

Dyeing Procedure

A weight "W" of fibres is boiled 15 minutes in 250 W distilled water containing the desired amount of dye. Thus for a 5% dyeing the weight of dye is .05W. A weight of salt equal to 50W is then added and boiling continued for 15 minutes, at the end of which the fibres are washed and air dried. A second procedure sometimes employed was to use a solution containing 10^{-4} g/cc., and such a small amount of fibre that the dye bath would not change concentration during the process. However, the exact manner of dyeing is relatively unimportant.

Why a Spiral Structure can be Observed

It seems a surprising result that this manner of fibre observation should lead to any sort of spiral measurement. Since all parts of the fibre, from the side toward the observer to the far side, fluoresce, and since just as much structure runs to the right as to the left, should not the curve minimum fall on zero? The observed light must be a conglomerate from all parts. If they all contributed equally to the image there should be no displacement of the curve minimum from zero. Since displacements are observed, it is obvious that some parts of the fibre are much more effective than others in determining the properties of the light.

The most obvious explanation is that the part in focus determines the characteristics of the fluorescent radiation. A few experiments on the depth of focus, and curves taken on the same fibre with varying positions of focus, showed that the position of focus plays a minor role. It is an interesting point that the microscope is not used in the usual manner here. Ordinarily one is interested in shape and in detail, and of course these properties can only be observed in objects lying in the focal plane. Here we are interested in intensity and in the total amount of light coming from a certain area of the fibre image next to the comparison mirror. Experiments showed that the parts not in focus contribute about as much as do those which are in focus.

The major cause for the appearance of spiral characteristics is that the doubly refractive nature of the front surface causes light passing through it, and having initially the directional characteristics of some other part of the fibre, to lose its original properties and become more representative in directional properties of the front wall. Closely lying layers of material with differing spiral angles are not differentiated. The result is an average or net spiral of the outer portion of the fibre. Other minor factors are the absorption and scattering of light from the far side of the fibre as it passes through the near (observer) side, and unequal excitation throughout the fibre. However, a proof based only on the theory of these complicated factors would not justify confidence in the spiral results. We turn to experiment:

Two hemp fibres were mounted on a slide, crossing each other at an angle of 54°. At the point of crossing they were in contact. Since hemp fibres have practically no spiral, the area where the two crossed represented a simplified fibre having a spiral of 27°. An examination of this crossing should give an idea of the extent to which the front and back parts of a fibre can annul each other, or to what extent the front surface determines the minimum point. The experimental curve is shown in Fig. 18, with the

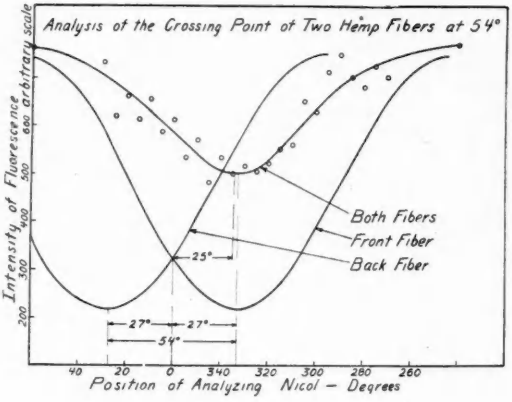


FIG. 18.

minimum falling at 25°. The curves for each of the two fibres are also shown. It is evident that the spiral value is determined by the front fibre.

The polarization of light from the crossed area was 15%, while that of either fibre alone was about 45%. This large drop is to be expected when we are dealing with a large spiral angle. To state accurately what happens to the light which originates in the back fibre and traverses the front fibre to reach the eye, requires a complicated treatment of the phase differences produced before the light emerges from the back fibre, those produced in the front one, the angle between the two and the wave lengths represented in the fluorescent band. In general, however, the elliptically polarized light produced in the back fibre emerges from the front fibre

with the major axis of the ellipse no longer parallel to its first direction, but shifted toward the direction of the front fibre. The two axes also emerge more nearly equal. In examining the system of two fibres we observe light which is a sum of the unchanged light from the front one and the distorted light from the back one. Since the distorted light would appear to be somewhat depolarized, when viewing it through one nicol, and since what directional properties it still possesses are more in the direction of the front fibre, the greatest effect on the total light is an apparent lessening of the polarization, with the spiral angle relatively unaffected. Thus percent. polarization results on a fibre such as sisal are probably lower than the real orientation.

If the spiral angle approaches 45°, so that the fibrils cross at a right angle, the polarized components from the back fibrils are transmitted unaffected through the front ones, and the resultant light from the two sets of fibrils thus appears unpolarized. This phenomenon appeared experimentally in the examination of yucca and coconut fibres. Fig. 19 is a picture of a yucca fibre, near the end, showing markings running in two directions distinctly not parallel to the axis, indicating a spiral structure. Fig. 20 is an X-ray diffraction photograph of a bundle of yucca fibres.

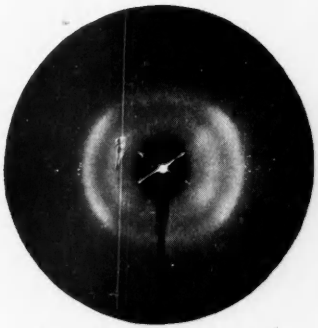


FIG. 20. Yucca; Cu Kα

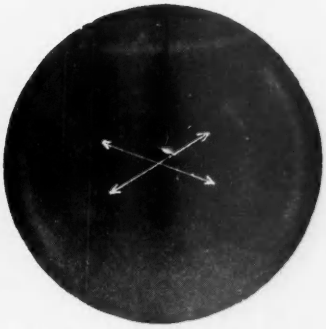


FIG. 21. Twisted ramie fibres; Fe Kα and β.

The strong arcs can be seen to have intensity maxima in the directions indicated by the arrows. This phenomenon of two maxima in place of one is indicative of a well marked spiral structure. Figs. 21 and 22 are attempts to produce the same phenomenon by introducing an artificial spiral. Fig. 21 was produced by a twisted bundle of ramie fibres, Fig. 22 by twisted hemp. It is very evident, then, that yucca is a fairly well oriented fibre with a spiral angle of 30–40°. Very little polarization was observed optically. The method breaks down when dealing with fibres of large spiral. Returning to Fig. 20, of yucca, it is interesting to note a number of small spots over the picture, which appeared whenever yucca was used, but not with other fibres. These spots were probably made by the small inorganic (calcium oxalate?) crystals which are sometimes found within the bundles of woody fibres.

Fig. 23 shows the pattern of coconut fibres, with a spiral of some 45° in evidence. Not a trace of fluorescent polarization could be found. Orientation and spiral are thus linked together in a curious fashion and produce effects difficult to separate by experiment. Thus we have seen that for cases of moderate spiral, regardless of orientation, the fluorescent method is highly successful, but when the spiral becomes large the percent. polarization is lowered. Without independent information it could not be determined whether the reduction was due to the spiral or to an actual

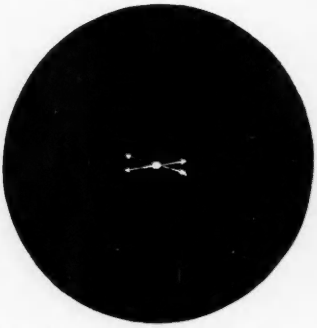


FIG. 22. Twisted hemp fibres; Cu Kα.

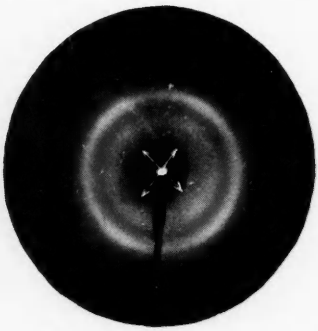


FIG. 23. Coconut fibre bundle; Cu Kα.

lowering of the orientation. For cases of low spiral the X-ray method is not of much help in determining spiral properties, but with large spiral and fair orientation it is very useful. This supplementing of the two methods is indeed fortunate.

Acknowledgments

Professors E. M. Chamot and S. H. Gage, by their kindness in giving me the use of needed microscopic equipment, and by assisting in a number of other ways, have been of great service to the Textile Foundation and myself. The same may be said of Professor Murdock and Dr. Fankuchen of the Physics Department, who have been very generous in allowing me to use their X-ray diffraction outfits, and of Professor Ernest Merritt, Head of the Department of Physics, for his guidance in the research and the granting of full use of the departmental facilities.

References

1. D. R. Morey. "The Measurement of Molecular Orientation in Fibres." *Tex. Rsch., 3,* 325 (1933).

2. A. Herzog. Die Unterscheidung der Flachs-und Hanffaser. Julius Springer, Berlin (1926).

3. W. A. Sisson and G. L. Clark. *Ind. and Eng. Chem., Anal. Ed., 5,* 296 (1933).

4. Meyer and Mark. Der Aufbau der hochpolymeren organischen Naturstoffe. Leipzig (1930), p. 104.

The Thermodynamics of Swelling

By RAYMOND L. STEINBERGER *

(*Continued from Vol. IV, No. 10*)

Entropy Changes With Swelling

Just as the integral heat of swelling W(i) has been defined we can define an integral free energy $\Psi(i)$ whose rate of change with (i) is the differential free energy ψ (i) already discussed. Since in the actual measurement of W(i) the total work done by the gel in expanding against the atmosphere is very small compared with W(i) the change in internal energy is equal to W(i) and, from the definition of the thermodynamic potential function, the free energy of Helmholtz, we have

$$\Psi(i) = W(i) - T\ S(i)$$

where S(i) is the integral change of entropy of mixing. The temperature is T, and, since all the swelling processes here considered are assumed to take place isothermally, we can write the relation between the differential quantities

$$\psi(i) = w(i) - T\ s(i)$$

where the change in entropy of a very large quantity of gel of swelling degree (i) is s(i) when it takes up one additional gram of water. If, at any given concentration, W(i) were precisely equal to $\Psi(i)$ the swelling gel would be able to perform work with 100% thermal efficiency by taking in water, and the entropy of mixing S(i) would be zero. The statement that the entropy becomes zero is slightly misleading. More exactly S(i) is not the absolute entropy, but is the change in entropy of the system comprising two isolated substances: one gram of perfectly dry gel and (i) grams of water, both at the same temperature, when the two are mixed isothermally. If S(i) were zero for every value of (i) the $\Psi(i)$ and W(i) curves would coincide. If the slopes $\psi(i)$ and w(i) were equal at every value of (i) the integral curves $\Psi(i)$ and W(i) would not coincide but would run parallel, and the differential entropy change s(i) would be zero. That is, S(i) would be constant regardless of the amount of water added to one gram of dry gel. This is impossible over the whole (i) range, for the W(i) and $\Psi(i)$ curves are zero at the zero value of (i). The differential quantities $\psi(i)$ and w(i) may however be approximately zero over a small range. That is, if a large amount of gel is swollen the amount (i), the addition or subtraction of a small amount of water is accompanied by a large efficiency of conversion of thermal energy into mechanical

* Dr. Steinberger is a Senior Fellow of the Textile Foundation working under the direction of Prof. P. W. Bridgman, Harvard University, Cambridge, Mass.

energy. This is probably the state of affairs in contracting muscle, for it is known that muscles perform work with a much greater thermal efficiency than that of the best artificial heat engines. It will be pointed out later that, in the case of dilution of NaOH solution, $\psi(i)$ and $w(i)$ are approximately equal over a small concentration range near $i = 2.3$ g water per gram of NaOH.

In an investigation of swelling phenomena in several gels, including cellulose, Katz [10] found that if (i) were changed over a certain interval the corresponding changes in ψ and w were equal, and erroneously concluded (see Fricke and Lüke [11]) that the integral free energy $\Psi(i)$ and heat of mixing $W(i)$ were equal. From the equation $\psi(i) = w(i) - T\ s(i)$ we can write $\Delta\psi = \Delta w - T(s_2 - s_1)$ for a change in (i) from i_1 to i_2. If $\Delta\psi = \Delta w$, Katz's results merely mean that the rate of change of entropy of mixing $S(i)$ is the same at both ends of the interval $i_2 - i_1$. That is $s_2 = s_1$.

Sufficiently accurate measurements of ψ and w have not yet been made on gels to allow reliable computation of efficiency to be made. Swelling pressure has so far been successfully measured only at high water contents; thus ψ can be computed directly from swelling pressure only in a narrow range near saturation. But because of the asymptotic nature of the $W(i)$ curve this is the range in which $W(i)$ and its derivative $w(i)$ are determined with the greatest uncertainty. To compare ψ and w over the lower range of i, ψ must be computed indirectly from the vapor pressure formula

$$\psi(i) = -(RT/M)\ \log\ p(i)/p_s$$

Fricke and Lüke,[11] in extending Katz's work, determined $w(i)$ in two ways: (a) from the calorimetrically determined integral heat $W(i)$, and (b) from the Kirchhoff formula for liquid mixtures—

$$w(i) = (RT^2/M)\ d(\log\ p(i)/p_s)/dT$$

and found fair agreement by the two methods. The indirect computation of ψ and w from vapor pressure data has several disadvantages. The derivation of the formulas assumes a perfectly homogeneous system like a true solution, and not the heterogeneous mixture of solid particles and liquid which exists in a gel. In most gels the determination of the swelling isothermal (p versus i) is complicated by hysteresis, which is characteristic of most systems in which one or more of the reacting constituents remains in the solid state. The vapor pressure assumes a higher value if equilibrium is approached with falling water concentration than if it is approached from below.

Fricke and Lüke have determined the differential heat $w(i)$ and free energy $\psi(i)$ relations for several gels,[11] and also for several true solutions.[12] In order to bring out the similarity in the behavior of gels and solutions their data for a typical example of each class are replotted in Fig. 2 (swelling of casein in water), and Fig. 3 (dilution of NaOH solution). In Fig 2 the calorimetrically determined values for $w(i)$ are plotted because the method is subject to less experimental error, but the free energy plotted was determined from vapor pressure measurements and is subject to considerable error because of hysteresis. The arrows indicate the direction in which equilibrium was approached.

In NaOH solution the ψ and w measurements are more accurate, for here we have to do with a homogeneous liquid system and hysteresis phe-

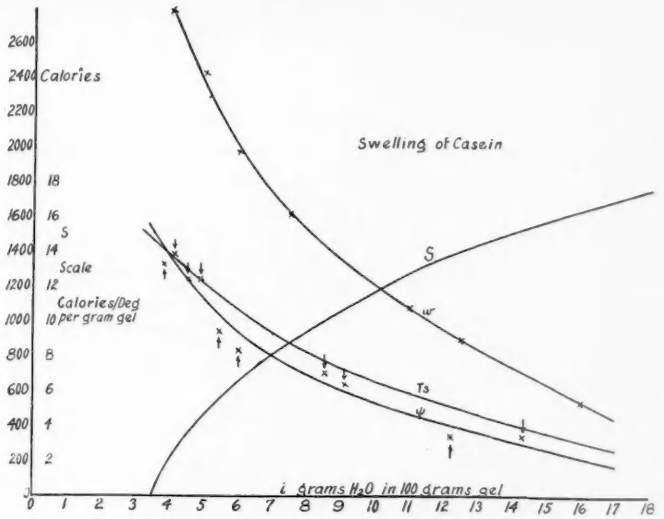


FIG. 2

nomena do not enter. The principal abscissa in Fig. 3 gives i in grams of water per 100 grams of NaOH in order to make comparison with the curves for casein more direct. Note that, whereas in casein the water content ranges from 3 to 17 grams per 100 grams casein (2.9 to 14.5% water), the NaOH solution is many times more dilute. The water content ranges from 100 to 440 grams water per 100 grams NaOH (50 to 82% water). The range of dilution is such that the ψ and w curves cross within it. Whether or not this will happen in gels with further dilution is not yet experimentally established.

The quantity Ts was determined graphically with the use of the free energy relation

$$\psi = w - Ts$$

The curve for the integral entropy change S(i) was determined by graphical integration of the Ts(i) curve. The zero of the S curve in each mixture is arbitrary. The absolute value cannot be determined until the ψ and w, or the Ψ and W, curves are extended down to $i = 0$. The zero value of S is arbitrarily set at the lowest value of i attained in each series of experimental data. In both mixtures the value of s falls continuously with increasing (i). It should, however, not be concluded that, because of decreasing s, the formation of a gel from the pure isolated constituents violates the First Law with a free energy which is greater than the loss in internal energy of the system. The total entropy change S with mixing is always positive, as shown in the graphs. If a very large quantity of perfectly dry gel is isolated from *one gram* of water the two constituents form a sys-

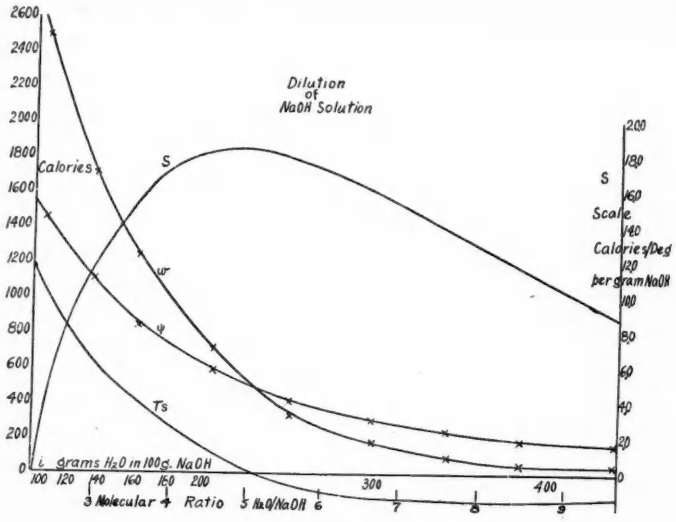


FIG. 3

tem with a definite total entropy. If the two are mixed isothermally the entropy of the system increases by a definite and large amount, measured by the separation of the ψ and w curves at $i = 0$ divided by the temperature. If to the large quantity of gel which now contains one gram of water another gram is added a further increase in entropy will take place, but the change will be less than for the first gram and so on for further dilution. If swelling were an inert process thermodynamically, the S(i) curve would be horizontal at the entropy of the isolated constituents. The process would be similar to the isothermal mixing of isolated quantities of the same kind of pure homogeneous substance, say water.

When a gel absorbs water the changes in entropy are associated with the mobile constituent water, rather than with the gel which is a solid incapable of molecular rearrangement. The addition of a small quantity of water to a very great quantity of perfectly dry gel represents a high degree of dispersal of the water molecules, the separation of which may be assumed as large as we please by choosing (i) sufficiently small. Taking entropy as a measure of the degree of haphazardness of the system as a whole the mixing process may be described as follows: The first water molecule to enter the perfectly dry gel, say, cellulose, has a choice of all the adsorption spots presented by the surface lattices of the micelles. The second added molecule has a choice of all but one adsorption spot, and so on with further dilution. As more adsorption spots are occupied the water molecules are compelled to take up a systematic distribution according to the arrangement of the spots; that is, according to the surface lattice of the micelles. The random distribution of the water decreases as (i) in-

creases. The maximum increase in entropy of the system, expressed per gram of water content, is to be expected with the addition of the first water to the perfectly dry gel. The term "adsorption spot" used here refers to the single atoms of the surface lattice which are effective in adsorption in the manner proposed by Langmuir:[13, 14] "There is good evidence that the forces which hold adsorbed substances act primarily on the individual atoms rather than on the molecules. When these forces are sufficiently strong it may happen that atoms leaving the surface become paired in a different manner from that in the original molecules. In a heterogeneous reaction (viz., swelling of a gel) the activity of a surface depends in general upon the nature, arrangement and spacing of the atoms forming the surface layers. The atoms forming the second layer below the surface are of importance only insofar as they determine the arrangement of the surface atoms." The micelles are certainly crystalline in the case of cellulose and its derivatives and present surface lattices to which water molecules can readily attach themselves in a systematic manner. Even if the micelle consisted simply of one of the long principal valence chain molecules characteristic of swelling bodies, there would be an appreciable systematic arrangement of the water molecules when they attach themselves to the relatively enormous gel molecule at certain definite and regularly spaced intervals.

In the solution of NaOH and water the ψ and w curves cross at $i_x = 230$ grams water per 100 grams NaOH, with the result that here s is zero. The total entropy of mixing is stationary with small changes in i above or below i_x. Above i_x the Ts curve is negative. The entropy of mixing becomes less with increasing water content, in spite of the fact that the amount of mass entering the reaction becomes greater. For example, the total entropy change when 230 g. water are mixed isothermally with 100 g. NaOH is 1840 calories per degree, but when 410 g. water are mixed with 100 grams NaOH the entropy change is 1040 calories per degree; 800 calories per degree less. In terms of molecular proportions the increase in entropy per molecule of NaOH is greater when water and NaOH are mixed in the ratio of five molecules of water to each molecule of NaOH than when the ratio is nine of water to one of NaOh. Fricke and Lüke[11] claim to have found in the swelling of agar and casein at high water contents conditions similar to the above for NaOH solution where ψ is greater than w.

When one gram of water is added to a very large quantity of gel of swelling degree (i) the change in entropy s(i) per gram of added water does not necessarily involve the specific molecules added. It involves the whole system, gel plus water, but is only expressed in terms of the added gram. Falling s(i) means that not only the water added, but also all the water already present in the gel, co-operates in the change s(i) in entropy. The added molecules may take the place of others already bound to adsorption spots, while the displaced molecules then move to unoccupied spots. The net effect, however, after the system, which involves gel, adsorbed water, and water vapor at a definite pressure, has settled down to equilibrium, is that new water molecules have on the average been added to unoccupied spots; equilibrium is kinetic. There is an interchange between vapor and adsorbed water molecules. Equilibrium exists when in unit time just as many vapor atoms condense on the adsorption spots as evaporate from them.

A quantitative expression for the ratio of the number (N_a) of atoms bound to adsorption spots, to the number (N_f) of atoms free in the vapor

phase per unit volume of the vapor, has been set up by Mark.[15] The expression for the ratio is

$$N_a/N_f = [N_o S\ \sigma \exp.\ (-e_1/kT)]/ [S\ \sigma\ N_f \exp.\ (-e_1/kT) + n \exp.\ (-e_2/kT)]$$

where the symbols have the following definitions:

N_o = the total number of adsorption spots in the gel.
S = number of collisions per square cm. per second on the surface, when the concentration in the vapor phase is unity.
σ = the area of activity of each adsorption spot.
n.—Each bound atom vibrates about a position of equilibrium in its adsorption spot with the frequence n.
exp. $(-e_1/kT)$.—Not all atoms which strike the surface have the proper energy to become bound to the surface. A certain amount of activity heat (e_1) is necessary. The probability of binding is expressed by this exponential factor where k is the gas constant per atom and T is the absolute temperature.
exp. $(-e_2/kT)$.—In the same way that a certain activation energy (e_1) is necessary before an atom can become bound to the surface, the bound atom must possess a definite activation energy (e_2), before it can leave the surface. The probability that the atom may evaporate is expressed by this exponential term.

The preceding expression for the ratio of N_a to N_f shows how the reacting atoms of the mobile constituent are divided between bound and free. The ratio depends on the temperature and the activity heats e_1 and e_2, and thus is general for any type of reaction and should hold whether adsorption is due to weak dipole forces or to strong principal valence forces.

Volume Contraction

It has been mentioned elsewhere that there is a measurable volume contraction with swelling. The volumes of the reacting constituents are not additive. If one c.c. of dry gel absorbs 0.1 c.c. of water the volume of the swollen gel is not 1.1 c.c. but is slightly less. The volume contraction C, expressed as c.c. per gram of dry gel, depends on the degree of swelling (i) according to the empirical relation given by Katz [1]

$$C = fi/g + i$$

where g and f are constants of the reacting material. To be consistent in terminology C is the integral (*i.e.*, total) contraction associated with the addition of (i) grams of water to one gram of dry gel. The corresponding differential contraction $c = dC/di$. For water swelling the ratio of C to W is the same order of magnitude for a number of gels when (i) is small. The same holds for the ratio of the differential quantities c and w. The ratio of c(o) to w(o) varies between 10×10^{-4} and 32×10^{-4} for the six swelling gels examined by Katz. The differential contraction c(o) is

the amount one gram of water shrinks when it enters a very large quantity of dry gel. The specific volume of the water suffers a reduction of about 30%. This means either an attraction between the water and dry gel of sufficient magnitude to compress the adsorbed film, or a change in degree of association of the water. The first seems the less probable, for the pressure would have to be very great and also at high states of dryness probably no continuous adsorbed film exists. It is known that at room temperature 80% of the liquid water molecules are double and occupy more than twice the volume of a single molecule. If there is a change from the mixture of double and single molecules to a pure single molecule water in the adsorbed layer there will be a reduction in volume of the water by dissociation alone.

Swelling and Capillary Theories

Thermodynamic treatment of swelling leads to necessary relations between certain measurable magnitudes without regard to the details of the fundamental processes involved. As soon as one abandons thermodynamic methods, and attempts to describe swelling phenomena in terms of molecular structure and intermolecular forces, one is led immediately into the theories of the formation of interfacial layers and into the complexities of colloidal and capillary chemistry. There are three types of layers of transition between phases which are present in a simple swelling system in equilibrium: The layers exist between the phases (a) liquid-vapor, (b) solid-vapor, (c) solid-liquid. The study of the liquid-vapor layer involves a knowledge of the theory of liquids and of gases far below the critical point; *i.e.*, vapor. The theory of liquids is very complex and is as yet only imperfectly developed. The solid-to-vapor interface has to do with gaseous adsorption for which an expression has just been given. The solid-liquid interface is the most complex. In a swelling process, beginning at the very dry condition of the gel, the first step is apparently one of true adsorption in Langmuir's sense, where the vapor (or gas) molecules condense upon the adsorption spots of the surface lattice of the micelles. The next step is probably the formation of a continuous film of liquid adhering to the already adsorbed molecules by dipole forces which are weaker than the bonds of the adsorbed molecules.

The problem of the liquid-vapor interface is very old and to date is still not completely solved. Recent studies have been based upon van der Waal's equation, which is assumed to hold in the homogeneous liquid and vapor phases and also within the transition layer between these two phases. Within a liquid and its vapor below the critical point the mutual attraction of the molecules modifies the equation of state. Also the volume of the molecules becomes an appreciable factor. In van der Waal's equation both are taken into consideration

$$p + a\rho^2 = RT/(V - v)$$

or in an abbreviated form

$$p + M = \Theta$$

p is the external pressure which is isotropic within each homogeneous phase. In a closed vessel in which a liquid is in equi-

librium with its vapor, p is the ordinary vapor pressure or the pressure the walls must exert to hold the volume of the system constant.

M is the molecular pressure which cooperates with p in tending to reduce the volume of the entire system. It is a consequence of molecular attraction and has a constant value throughout a given homogeneous phase but has a value greater in the liquid than in the vapor.

Θ is the kinetic pressure; a function of the molecular thermal motion, and tends to increase the volume of the system. It is a function of the temperature and density.

Van der Waal's equation is simply a statement of the equilibrium of the three forces p, M, Θ acting normal to a unit area drawn within the system. K. Fuchs [16] was the first to assume that this equation not only holds in the homogeneous phases, but also in the transition layer between liquid and vapor, and that in the layer a non-isotropic pressure condition exists. The thermal pressure Θ is isotropic everywhere throughout the whole system. The molecular pressure M has a value M_1 in a direction normal to the interface different from the value M_2 parallel to the interface. All points for which $M_2 - M_1 \neq 0$ belong to the liquid-vapor interface. Since Θ is isotropic and M is not, p also must be non-isotropic within a given transition layer. We have therefore three expressions for van der Waal's equation: (a) In the homogeneous phases $p + M = \Theta$. (b) In the transition layer, when pressures are measured normal to the interface, $p_1 + M_1 = \Theta$. (c) Parallel to the interface $p_2 + M_2 = \Theta$. The external pressure p_1 normal to the interface is different from the pressure parallel thereto, so that within the layer there is a departure from the law of Pascal measured by the difference $p_1 - p_2$. Laplace's capillary constant σ is then the integral of $p_1 - p_2$ over the layer of thickness h, i.e.,

$$\sigma = \int (p_1 - p_2)\,dh$$

Bakker [17] and Hulshof [19] computed the capillary constant σ from certain plausible assumptions. Hulshof computed the molecular forces M_1 and M_2 and then, from the two van der Waal's expressions just noted, p_1 and p_2 were determined. The results for the two molecular pressures are

$$M_1 = a\rho^2 + c_2\rho d^2\rho/dh^2 - (c_2/2)\ (d\rho/dh)^2$$

$$M_2 = a\rho^2 + (c_2/2)\ \rho\ (d^2\rho/dh^2)$$

And the difference then is

$$p_1 - p_2 = M_2 - M_1 = -(c_2/2)\ \rho\ (d^2\rho/dh^2) + (c^2/2)\ (d\rho/dh)^2$$

Before M_1 and M_2 can be known, not only must the density ρ be known at all points of the interface, but both the first and second derivatives of ρ with respect to the normal to the interface must also be known.

By considerations of the energy changes of unit mass in the transition layer Hulshof [20, 21] has shown that

$$(p_1 - p) = 2 \int \rho de'$$

and

$$(p_2 - p) = \rho e'$$

where e^1 is the amount the energy per unit mass at a given point in the transition layer exceeds the energy per unit mass in the homogeneous phase where the external pressure is p. From the two energy expressions and the fact that the total free energy of the system must be a minimum it can be shown that

$$e - TS + p_2 v = Z = \text{constant}.$$

The constant Z is the Gibbs' potential. For the entire system, then, the conditions for equilibrium are:

(1) Constant temperature and the same temperature at all points.
(2) The pressure p_1, normal to the transition layers, is the same at all points and is equal to the pressure p in the homogeneous phases.
(3) Gibbs' potential (Z) is constant throughout the entire system including the transition layers. In the transition layers it is the tangential pressure p_2 which enters the expression for the potential. In the homogeneous phases p_2 becomes equal to p.

Swelling and Imbibition. [Hulshof[22]]

If, in a body whose surface is wetted by a liquid, very narrow openings, whose width is less than twice the thickness of the transition layer, exist, the liquid will, if it is admitted at all, be drawn forward into the capillaries with great force because of the tangential pressure p_2. The openings are assumed to be so narrow that no free liquid surface can appear, and thus p_2 is not diminished by the appearance of surface tension forces. In addition to the pressure p_2, which draws the liquid into the pores, the liquid will exert considerable pressure (π) normal to the walls. This is true swelling pressure. It can be shown by a simple thermodynamic device that the swelling pressure π, normal to the walls of a crevice of width 2h, is equal to the tangential pressure p_2 at the distance h from either wall. The pressure p_2 has a definite value (the value at the perpendicular distance h in a free layer) regardless of whether the other wall is present or not.

Consider two identical plane surfaces (Fig. 4) of width b and length a arranged parallel to each other at a separation 2h. Consider the plates wholly immersed in a liquid, capable of wetting the surfaces, under no external pressure. The liquid may be expelled from the space between the plates by either of two isothermal and reversible processes. By means of

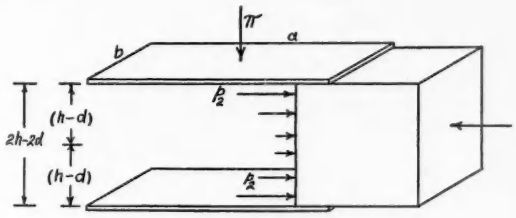


FIG. 4

some external mechanical device let a pressure π be exerted normal to the plates, pressing them together by the small amount 2d. The amount of liquid contained in the volume 2 abd will be pressed out. The work done by the external device will then be 2 $\bar{\pi}$ abd, where $\bar{\pi}$ is the average value of π over the interval d of h. The liquid then remaining can be removed by pushing a piston of dimensions 2(h — d) b between the plates for the distance a. This piston is opposed by the tangential pressure p_2, which is a function of the distance from the plate to the point where p_2 is measured. The work done by the piston on the system is then

$$2ab \int_0^{h-d} p_2 dh$$

The total work done in expelling the water by this first process is then

$$2\bar{\pi}abd + 2ab \int_0^{h-d} p_2 dh$$

The liquid may also be expelled from the undisplaced plates (*i.e.*, when $\pi = 0$) by one stroke of a larger piston of thickness 2h. The work in this case will then be

$$2ab \int_0^{h} p_2 dh$$

Since the configuration of the system at the end of each of the isothermal processes is identical, and they begin with an identical configuration, the work done by one process is equal to the work done by the other. Therefore we may write

$$2\bar{\pi}abd + 2ab \int_0^{h-d} p_2 dh - 2ab \int_0^{h} p_2 dh = 0$$

$$\bar{\pi}d = \int_0^{h} p_2 dh - \int_0^{h-d} p_2 dh$$

$$= \int_{h-d}^{h} p_2 dh$$

$$= \bar{p}_2 d$$

$$\pi = p_2$$

Since we may make the interval d of h as small as we choose, the point values π and p_2 replace the mean values $\bar{\pi}$ and $\bar{p}_2$. Therefore we have, that, if the plates are separated the distance 2h, h being less than the thickness of the transition layer of liquid which will form on a free surface of the plates, the swelling pressure π is equal to the value of the tangential pressure p_2 and the transition layer, at a distance h measured normal to the plate.

Hulshof [22] has pointed out that swelling pressure and osmotic pressure are identical. If a number of particles, ions, sugar molecules or colloidal particles, are placed in a vessel of water, each particle will surround itself with a transition layer of water. Between the particles themselves, and between the particles and the wall, a swelling pressure π will arise which

will be directed normally to the wall or to the surfaces of the particles. The particles will strive to distribute themselves uniformly throughout the water because of the swelling pressure. If two vessels A and B (Fig. 5) communicate by means of a wall m, permeable only to the solvent water, and there are a few more particles per unit volume in B than in A, there will be a flow of water from A to B through the membrane with a consequent rise in pressure in B. In other words, osmotic pressure will be set up. If A and B are to be in equilibrium, the Gibbs potential Z must be everywhere the same throughout both vessels, in the membrane and at each point of every transition layer. The flow of water from A to B will continue, in case the hydrostatic pressures in A and B are permitted to equalize, until, on the average, the transition layers surrounding all particles in both vessels will have attained the same thickness. The total external pressure P on one

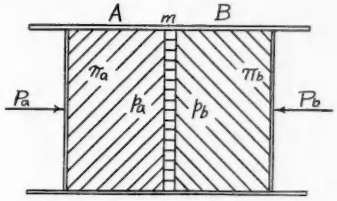


FIG. 5

compartment is the sum of the swelling pressure π and the pressure p in the homogeneous solvent, water. Then if the total pressures in the two vessels are not permitted to equalize, by holding the volume constant when we raise the concentration in B, we have, after equilibrium has been attained,

$$P_a = \pi_a + p$$

$$P_b = \pi_b + p$$

The pressure of the water p remains constant throughout. Then

$$P_o = (P_b - P_a) = (\pi_b - \pi_a)$$

The osmotic pressure P_o, or difference in total external hydrostatic pressure between the two vessels, is nothing other than a difference in swelling pressure exerted by the dissolved particles.

References

12. R. Fricke. "Verdünnungsarbeiten und Verdünnungswärmen im Gebeit Konzentrierter Lösungen." *Z. für Elektrochemie, 33,* 441–55 (1927).

13. I. Langmuir. "Constitution of Solids and Liquids." *J. Am. Chem. Soc., 38,* 2254–95 (1916).

14. I. Langmuir. "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum." *J. Am. Chem. Soc., 40,* 1361–1403 (1918).

15. H. Mark. Physik und Chemie der Cellulose. Springer (1932), P. 181.

16. K. Fuchs. "Directe Ableitung einiger Capillaritätsfunctionen." *Wiener Sitzungsberichte, 48,* 1362–91 (1889).

17. G. Bakker. "Zur Theorie der Kapillaritat." *Z. für physik. Chem., A33,* 477–99 (1900).

18. G. Bakker. "On the Theory of Surface Forces." *Phil. Mag., 20,* 135–57 (1910).

19. H. Hulshof. "The Direct Deduction of the Capillary Constant (σ) as a Surface Tension." *Amsterdam Kon. Akad, 2,* 389–98 (1900).

20. H. Hulshof. "Über Spannungen und Drucke in Granzflächen und Trennungsflächen eines Fluidums: Quellung." *Annalen der Physik und Chemie, 67,* 278–300 (1922).

21. H. Hulshof. "Die tangentielle Druck in Grenzschicten von Flussigkeiten." *Z. für physik. chem., A128,* 110–34 (1927).

22. H. Hulshof. "Quellungsdruck und Osmotischer Druck." *Amsterdam Kon. Akad., 33,* 165–75 (1930).

A Suggested Standardization of Breaking Strength Tests for Rayon Yarns

By Dr. IRVING J. SAXL *

Introduction

IT might appear obvious that the mean breaking strength of rayon and silk yarns, as determined by the arithmetic average of single strand breaking tests,† is a sufficient characteristic to settle the question as to whether a given lot should be accepted or rejected, in accordance with specifications. It is clear, however, that different lots which have the same mean strength may differ in the essential feature of minimum strength. Furthermore, a generally excellent lot may have one weak spot. What is necessary therefore seems to be a test which will determine, within reasonable likelihood, that a given lot shall have not more than a specified small percentage of yarn inferior to a given minimum breaking strength tolerance. For predicting from laboratory tests how the yarn is going to behave during processing, as far as breakage is concerned, *the total amount of breakage which must be expected in production is more important than one occasional weak spot.*

Brief reflection indicates that what is essential is that *not too great a percentage of the given lot should have a breaking strength less than a prescribed minimum.* The total occurrence of spots below the limit of tolerance is more characteristic for a yarn if it is to withstand, successfully, the resistance of processing than its mean average breaking strength or its weakest spot.

In order to apply such a condition, using samples consisting of not too large a number of individual specimens, one must appeal to the general principle of probability. The present paper

* Director Research and Development, The Waypoyset Mfg. Co., Pawtucket, R. I.

† The American Society for Testing Materials has adopted the 10″ distance between clamps and the 12″ per minute speed of the pulling jaw. These are now considered standard for rayon.

proposes a systematic and impersonal procedure, fair alike to buyer and seller and reducing the necessary amount of testing to a minimum.

Conclusions

This paper proposes a procedure, consisting of either one or two steps, depending upon the results shown by the first step. The first step consists of taking a sample of 10 specimens. The mean breaking strength and the standard deviation shown by this sample are computed. Using the normal probability law, an estimate is obtained for the probable percentage of the given lot which will show breaking strength, either in accordance with specifications or inferior to a specified minimum.

Three ranges for this percentage are considered. A percentage falling in the lowest range indicates a satisfactory lot (first quality); a percentage in the top range indicates a lot, so inferior as to merit rejection (inferior quality). When the percentage falls in the middle range, the original sample should be regarded as ambiguous and a larger sample should be taken (second quality). This ambiguous case leads to the use of the second step.

A new sample introducing 30 additional specimens is taken in this instance and the original process repeated for the total set of 40 samples. For this larger sample a more accurate estimate of the standard deviation is arrived at than possible on the basis of the original 10 specimens. A new division of the range of percentage is now made. For percentages in the lower range, the sample indicates that the original lot is now acceptable; in the upper range, the results merit rejection of the lot.

In drawing up specifications for a given standard of yarn, it will be necessary to specify:

First—A minimum breaking strength in grams.

Second—A division of the probable percentage range (of the given lot estimated to show the breaking strength inferior to the specified minimum into three subranges, first, second and inferior).

Third—Division of the range for the second sample into acceptable and unacceptable. For the sake of concreteness we may suggest, without claiming to insist upon the specific numbers mentioned, the following: 150 denier, 60 filaments, 250 grams as specified. The first quality yarn will show a probable percentage of yarn breaking at 250 grams or less, on less than ½ percent. of the total lot; second quality will show a probable breaking strength at 250 grams or less between ½ and 5 percent., while inferior quality shows an estimated probable breaking strength of 250 grams or less in excess of 5 percent. of the total weight. In the case of the second quality when 40 specimens are tested, acceptable quality is that which shows an estimated breaking strength of 250 grams for less than 2%. Unacceptable quality is that which our second test shows breaking strength of 250 grams for 2% or more.

Theory

In the theory of probability distributions, the first important constant is the arithmetic mean; a second is the standard deviation, σ. This latter measures the spread of the distribution. Higher moments will not be

considered here. In distributions approximating that of the normal probability law, there is a pronounced concentration near the arithmetic mean and the curve is symmetrical on either side.

Fig. 1 shows graphically the representative mean value of 100 actual observations and also the spread around this mean. The class interval is 10 grams. The curve obtained is essentially similar to a Normal Probability Curve.

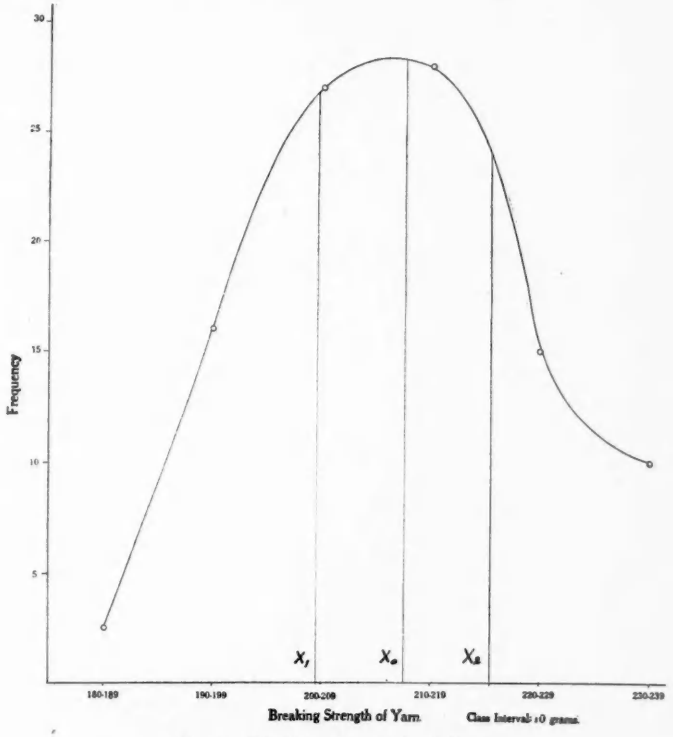


FIG. 1. Breaking Strength of Yarn.

There is, however, the characteristic difference between this and the Gaussian Distribution, in that the latter does not cut the axis of the abscissa in any point but only approaches it at infinity. In our instance, the curve appears to be definitely limited at the end of the lower breaking strength.

The technical interpretation of this statistical distribution means that a breaking strength below a certain minimum point, say 175 grams, does not exist practically.

It is assumed now that what makes a yarn technically valuable or not is primarily this amount of yarn that shows adequate strength. The yarn will break and show other deficiencies, particularly at the points of lower breaking strength, while the portion of high and highest breaking strength will not show undesired characteristics in spinning, throwing, weaving or knitting and will be in a position to pass the heddles and other points of resistance readily.

To give a characteristic picture of the yarn, it seems therefore to be of greater importance to know the percentage of the yarn that will fall below a certain critical minimum than just to know its arithmetical average.

Graphically speaking, the part for instance between the ordinate x_1 and the left side of the curve, would show the amount of yarn the breaking strength of which would fall below 200 grams. This is believed to be more characteristic for the technical quality of the yarn than the position of the arithmetic average x_0.*

This method permits one to estimate with a fair degree of accuracy the amount of difficulty a given lot will cause in regular production, due to probable breakage, etc., on account of a definite percentage of the total length of the yarn being below minimum requirements.

If, in accordance with this, in the buyer's specifications, it is specified that, say, not more than 3 percent. of the total yarn shall show a breaking strength below the technical limit of uniform production, *e.g.*, 200 grams, a means is given herewith of determining clearly, after receipt of a shipment of yarn, whether it complies with the standard of tolerance given in the order or not.

The data given above may be assumed as evidence that a distribution, approximating that of the normal probability law may be expected in the case of breaking strengths of yarn. The general theory of normal distributions is found in text books on the subject.†

The Normal Probability Curve

The normal probability curve may be written so as to involve two or three parameters, usually so taken that the mean occurs at the origin and the area under the curve is unity. If given data are to be compared with the probability curve, one naturally computes the mean of the given data and chooses this as new origin. One also divides the observed frequencies by the total frequencies, so as to reduce the problem to one of probabilities where the total probability is taken as one or certainty. There remains, however, the question as to the unit for abscissas. In connection with the tables here given this unit is to be taken as σ, which denotes the standard deviation. When the data are thus reduced, the determination of the percentage of area of the associated probability curve which shall lie to the left of a given negative abscissa may be read from Appendix Table 5.

* The arithmetic average would remain the same if the spread of the readings would be several times as wide as in the condition of the yarn indicated above. Still, the yarn with the wider spread will show more breakage in production than the one with the narrower spread, despite the fact that the arithmetic average of the breaking strength tests is the same in both cases.

† See References.

Application of the Method

To illustrate the proposed procedure three cases are considered; the first illustrating the case of acceptance, the second that of rejection and the third the ambiguous case, referred to above. This third example is then carried further, illustrating the use of the second step.

TABLE 1—ACCEPTANCE.

Columns (1) and (2) give the data as first obtained.

Specimen Number	*Observed Br. Str. in grams*	*Difference (d) from average value*	*Squares of Deviation*
1	300	—18	324
2	292	—26	676
3	325	+ 7	49
4	340	+22	484
5	300	—18	324
6	300	—18	324
7	294	—24	576
8	340	+22	484
9	350	+32	1024
10	340	+22	484
	3181		4749

Here, the total number of specimens is 10, hence the mean breaking strength is $3181/10 = 318$.

To determine σ, we must find the sum of the squares of the deviations from the mean. With reference to this, we have the deviations as shown in column 3 of Table I. The squares of the deviations given in column 3 are listed in column 4. The mean for column 4 is 474.9. This is the value of $\Sigma\, \sigma^2$.

Hence $\sigma = \sqrt{474.9} = 21.8$.

TABLE 2—REJECTION.

Specimen Number	*Observed Br. Str. in grams*	*Deviations from mean*	*Squares of deviations*
1	260	—10	100
2	250	—20	400
3	270	0	0
4	280	+10	100
5	285	+15	225
6	270	0	0
7	290	+20	400
8	250	—20	400
9	282	+12	144
10	260	—10	100
	2697		1869

The mean, $2697/10 = 270$.

$\Sigma\, \sigma^2 = 1869$; $\sigma = 13.7$.

Assuming 250 gms. as the critical lower limit for acceptance, we form the difference $318.1 - 250 = 68.1$. In terms of σ as a unit, this is a deviation of $68.1/21.8 = 3.1$ units. Referring to Table 5 we find for 3.1, the value .10%. This means that of the total .10 percent. lies below the given critical value, or one tenth of one percent. Hence the lot is accepted without further testing. Any such observed percentage less than that stipulated in the accepted standards, say ½ percent., would have meant acceptance.

Using the previous critical value of 250, we get for the observed deviation from the mean, $270 - 250 = 20$. In terms of σ units, this is 1.5. From Appendix Table 5 we find for 1.5, that 6.7 percent. of the lot may be expected to break at less than the specified strength of 250 gr. The yarn is therefore rejected. Any percentage in excess of a specified maximum (say 5 percent.) would have been rejected.

TABLE 3—AMBIGUOUS CASE.

Specimen Number	*Observed Br. Str. in grams*	*Deviations from mean*	*Squares of deviations*
1	310	+19	361
2	340	+49	2401
3	300	+ 9	81
4	280	—11	121
5	285	— 6	36
6	270	—21	441
7	260	—31	961
8	292	+ 1	1
9	270	—21	441
10	300	+ 9	81
	2907		4865

The mean is $2907/10 = 291$.
$\Sigma\ \sigma^2 = 486.5$; $\sigma = 22.1$.

The deviation used is $291 - 250 = 41$. In terms of σ units, we have $41/22.1 = 1.85$. In Appendix Table 5 this yields 3.2 percent. Since this lies between ½ percent. and 5 percent., this first step remains ambiguous and a larger sample must be chosen, as in Table 4.

The deviation used is $294 - 250 = 44$. In terms of σ units we have $44/20.7 = 2.12$. In the table this yields 1.7%. Since this is less than 2%, the lot should be accepted.

The procedure follows the same routine as before save that now the number of specimens is 40. For this more extensive sample we leave no ambiguous range, but accept all lots for which the estimated percentage of specimens breaking at less than 250 gm. (the previously used standard) is less than 2%, rejecting all those for which this percentage is at or above 2%.

In conclusion, the writer wishes to express his sincere appreciation to Prof. A. A. Bennett for his assistance and suggestions in compiling this paper.

TABLE 4—CLARIFICATION OF TABLE 3.

Specimen Number *	*Observed Br. Str. in grams*	*Deviations*	*(Deviations)²*
1	310	+16	256
2	340	+46	2116
3	300	+ 6	36
4	280	—14	196
5	285	— 8	64
6	270	—24	576
7	260	—34	1156
8	292	— 2	4
9	270	—24	576
10	300	+ 6	36
11	256	—38	1444
12	290	— 4	16
13	308	+14	196
14	270	—24	576
15	320	+26	676
16	280	—14	196
17	290	— 4	16
18	260	—34	1156
19	296	+ 2	4
20	308	+14	196
21	284	—10	100
22	320	+26	676
23	286	— 8	64
24	310	+16	256
25	290	— 4	16
26	324	+30	900
27	300	+ 6	36
28	330	+36	1296
29	270	—24	576
30	308	+14	196
31	320	+24	576
32	300	+ 6	36
33	260	—34	1156
34	290	— 4	16
35	322	+28	784
36	276	—18	324
37	300	+ 6	36
38	288	— 6	36
39	310	+16	256
40	276	—18	324
	11,750		17,152

The mean is $11,750/40 = 294$. gm.

$\Sigma\ \sigma^2 = 428.8$; $\sigma = 20.7$.

* The first ten of these specimens are those used in the previous test.

Appendix Table 5

Area Under the Normal Probability Curve

x/σ is the deviation from the middle ordinate x_0 in Fig. 1 in terms of standard deviation units. A is the area under the curve from the middle ordinate to x. These areas have been computed [1, 8] for one-half of the curve only, on account of the fact that the curve is symmetrical. % denotes the percentage area lying beyond the given value of x/σ.

x/σ	A	%	x/σ	A	%
0.0	.00000	50.0	2.0	.47725	2.3
0.1	.03983	46.0	2.1	.48214	1.8
0.2	.07926	42.1	2.2	.48610	1.4
0.3	.11791	38.2	2.3	.48928	1.1
0.4	.15542	34.5	2.4	.49180	.82
0.5	.19146	40.9	2.5	.49379	.62
0.6	.22575	27.4	2.6	.49534	.47
0.7	.25804	24.2	2.7	.49653	.35
0.8	.28814	21.2	2.8	.49744	.26
0.9	.31594	18.4	2.9	.49813	.19
1.0	.34134	15.9	3.0	.49865	.14
1.1	.36433	13.6	3.1	.49903	.10
1.2	.38493	11.5	3.2	.49931	.07
1.3	.40320	9.7	3.3	.49952	.05
1.4	.41924	8.1	3.4	.49966	.03
1.5	.43319	6.7	3.5	.49977	.02
1.6	.44520	5.5	3.6	.49984	.02
1.7	.45543	4.5	3.7	.49989	.01
1.8	.46407	3.6	3.8	.49993	.007
1.9	.47128	2.9	3.9	.49995	.005
			4.0	.49997	.003

References

1. J. C. MacKinnon. Notes on Elementary Statistics. M. I. T., Sept., 1933.
2. Professor Mansfield Merriman. The method of least squares. John Wiley & Sons, New York.
3. E. Baecklin. The limits of the Gaussian probability function. *Nature*, 1929, 123, 409.
4. C. V. L. Charlier. Vorlesungen Ueber die Grundzuege der mathematischen Statistik.
5. Mills & Davenport. Problems and Tables in Statistics. Pp. 129. Henry Holt & Company (1925).
6. Dr. R. H. Pickard. Statistical Methods in Industry. *Tex. Mfr.*, 470–71 (1933).
7. A. E. Dufton. Statistical Data. Plotting of Frequency Distribution. *Proc. Phys. Soc., 46*, 47–50 (1934).
8. W. Edwards Deming. On the Application of Least Squares. *Phil. Mag.*, Vol. 11, P. 804–29.

Abstracts

This section is compiled under the direction of the Committee on Abstracts and Bibliography: Prof. E. R. Schwarz, Chairman, Dr. W. E. Emley, Prof. Louis A. Olney and M. W. Weiss.

I. Fibres (Synthetic and Natural) and Fibre Analysis

Cotton Cellulose: Dissolution of Chemically Modified in Alkaline Solutions. G. F. Davidson, *J. T. I.*, May, 1934, P. T174–T196.

The results described in the present paper show that the solubility of hydro- and oxy-celluloses at any temperature is a maximum at a certain alkali concentration, and, as the temperature is lowered from the normal, the maximum solubility is greatly increased and occurs at a lower alkali concentration. When modified cotton is boiled under pressure with dilute alkali, the residual material is more soluble in sodium hydroxide solution at —5° C. than the original modified cotton, in spite of the loss of weight that occurs during the boil. When a modified cotton is treated with 5N sodium hydroxide—a treatment that effects insignificant dissolution—and, after dilution of the alkali to lower concentrations, the solubility at low temperatures is determined, it is found that the maximum solubility is lower, and occurs at a higher alkali concentration, than with the modified cotton not previously treated with the 5N alkali. The solubility of any modified cotton, measured under the optimum conditions at —5° C. is greater the greater its fluidity, samples with very high fluidities being completely soluble. By means of successive extractions with sodium hydroxide solutions under suitably chosen conditions, a hydrocellulose has been separated into four fractions differing in fluidity. It is shown that many of the experimental results can be explained on the following assumptions—(1) that cellulose acts as a very weak acid, forming salts with sodium hydroxide; (2) that modified cottons consist of mixtures of chain-molecules of different lengths, the average length decreasing with increasing modification; (3) that the tensile strength, the fluidity and the solubility of modified cottons are all functions of the chain length frequency distribution; (4) that before dissolution of a chain-molecule can occur, the cohesive forces binding it to its neighbours must be overcome by the swelling forces; (5) that the shorter chain-molecules are more easily detached in this way than the longer. Possible mechanisms to account for the alteration of the properties of hydro- and oxy-celluloses by an alkaline boil are also discussed. (8)

RAW SILK GRADING IN JAPAN. Leo Duran. *Am. Silk and Rayon J.*, June, 1934, P. 29–30.

The article is a generalized one involving several criticisms of the present system of grading raw silk. It points out the fact that the quality of raw silk cannot be determined by seriplane grading alone and the ninemeter test, while improving somewhat the evenness evaluation, has nothing to do with the nature of raw silk. The statement is further made that the so-called visual inspection together with knowledge of the source of supply, is of paramount importance. A number of examples are quoted from the author's experience in confirmation of these statements. He also points out the fact that no cocoons should be mixed, that is cocoons from any given district or groups of districts should be kept together wherever the characteristics of the raw silk are the same. He also recommends that the Japanese official testing house make it a rule not to accept any gummy silk unless the gums can be easily removed through light soaking. Further, they should not accept any bale of raw silk containing more than one color. (S)

RAYON: BEFORE PAPYRUS . . . BEYOND—. G. J. Esselen. *J. Franklin Inst.*, March, 1934, P. 217, 273–87.

The author presents an historical account of the uses and development of cellulose. (Copied complete from the *Eastman Kodak Abs. Bull.*, April, 1934.) (S)

USE OF COPPER-AMMONIA SOLUTIONS FOR THE DETERMINATION OF IMPURITIES IN (COTTON) LINTERS. A. P. Sakoshchikov. *Iskusstvennoe Volokno* (*Artificial Fibre*), 1934, V. 6, No. 1, P. 36–9.

Expose 1.5–3 g. of crude or refined linters to the fumes of HCl for about 1 min. and then to NH_3, wash, dry and dissolve in Schweitzer's reagent, filter, wash the insol. residue, dry and weigh. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3893.) (W)

VISCOSE: CAUSE OF "MILKY" SPOTS ON. Stefan Poznanski. *Russa*, 1934, V. 9, P. 179–83, 257, 259.

"Milky" spots in viscose are decreased by: (1) decreasing the amt. of CS_2 (even very slight differences can have a remarkable effect), (2) decreasing the viscosity of the viscose, (3) increasing the NaOH content of the viscose, (4) addn. of a small amt. of Na sulforicinate to the viscose, (5) increasing the H_2SO_4 content of the coagulating bath, (6) decreasing the $ZnSO_4$ content of the coagulating bath, (7) lowering the titer of the elementary fibres, (8) decreasing the no. of elementary fibres in the threads. From the results of microscopic examn. of sections of fibres produced from viscose with very high CS_2 contents (50, 60 and 70%), P. considers that the voids under the surface skin which cause "milkiness" are not due to a difference in the structure of the skin and of the central portion of the fibre (contrary to Preston, *Chem. Abs.*, V. 25, P. 4702–3), but to the retention of excess CS_2 within the fibre on coagulation, this CS_2 evapg. out through the surface on subsequent drying of the thread. Photomicrographs are given and discussed in support of this theory, and it is shown that the action of most of the factors enumerated above (except (6), the action of which remains as yet unexplained) agree with this hypothesis. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3893.) (W)

II. Yarns and Fabrics

Artificial Leather: New Processes for the Preparation of. *Kunststoffe*, March, 1934, P. 56–7.

The patent of Arthur H. Kilner, London (Ger. 584, 606), is considered and mention is made of the use of wool scrap for making artificial leather proposed by Barker of the Wool Industries Research Association, of Leeds. (Copied complete from the *Eastman Kodak Abs. Bull.*, April, 1934.) (S)

Artificial Silk: New Methods for the Investigation of. R. Flint. *Kunststoffe*, Feb., 1934, P. 32–4.

The principal physical methods for evaluating artificial silk, the control of its manufacture, and its dyeing qualities are described. (Copied complete from the *Eastman Kodak Abs. Bull.*, April, 1934.) (S)

Cloth Qualities: A Tactile Comparison of the—of Continental and Noble Combed Materials. Henry Binns. *J. T. I.*, May, 1934, P. T157–T173.

A second paper of a series of tests on the "handle" of cloths by the sense of touch. Information as to the stability of the individual judgment, the magnitude of fluctuations recorded, and the influence of touch seem worthy of record. The practical applications suggested by the tests carried out indicate that a sensitive touch correlates rather well with the judgment of fabrics based upon the usual measurable characteristics and determined independently by a number of skilled observers. They may indeed be the final arbiter. The author comments that to the wool trade as a whole the development of a sense of touch is decidedly important. Fundamental differences in cloth construction can be detected by the means described and apparently are not yet available by any mechanical or optical method of measurement. (S)

Cotton Yarn: Influence of Fibre-Length on the Proportion of Fibre-Strength Utilized in. Sigurd Kohler. *J. T. I.*, April 1934, P. T141–T149.

Several different experiments were carried out to give the relation between the strength of the cotton fibres and the yarn produced. By these experiments it is shown that the strength of the yarn is substantially 10 to 20% of that of the fibres, and these low values first depend upon irregularities in the count and the twist of the yarn. If specially regular and short pieces of yarn are chosen for experiments in the same way as, for example, certain other investigators have done, a considerably higher effect of efficiency may be obtained. In this paper a formula is developed to show the relation between the number of broken fibres, the length of slippage, and the average length of fibres. The formula appears to apply to yarn which has not been too loosely twisted; that is, to yarn containing approximately twenty or more turns per inch. It is also shown that the shorter the mean fibre length, the greater is the influence of the twist on the strength of the yarn. (S)

III. Chemical and Other Processing (Not Otherwise Classified)

Hydrogen-ion Concentration: Measurement of—in the Textile Industry. K. Schulze. *Mitt. Textilforschungsanst. Krefeld,* 1932, V. 8, P. 12–16.

An account of current methods. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2190.) (W)

Military Khaki. J. B. Prince. *Tiba,* 1934, V. 12, P. 181–9.

The process of making military khaki is described. The factors affecting the fastness of the shade were investigated. Conclusions: (1) With Cr sulfate and Fe acetate, excellent fastness to washing, Cl and sweat is obtained by using Na_2CO_3 at the boil as fixing agent and passing through the Mather-Platt after the hot flue. (2) Similar results are obtained with Cr formate; Cr acetate gives approx. the same fixation of Cr and Fe, but less satisfactory fastness. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 3238.) (W)

Naphthol Dyers: Note for—on the Prevention of Occupational Dermatitis. Hilton Radley. *Dyer,* 1934, V. 71, P. 127.

A light greasing of the hands and the wearing of comparatively tight-fitting cotton gloves over which are worn the usual loose-fitting rubber gloves are recommended. The cotton undergloves are not to be removed until the completion of the working period. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2909.) (W)

Oxidized Fatty Acids: Determination of—in Threads and Crepes. G. Baroni. *Boll. ufficiale staz. sper. seta,* 1932, V. 2, P. 100–3.

Oxidation of linseed oil on threads is fairly rapid at room temp.; max. oxidation is reached after one hr. at 110°. For the detn. of OH acids the fibres are boiled for one hr. with a soln. of neutral Marseilles soap. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2910.) (W)

pH Determination in the Dyeing Industry. Maurice Déribéré. *Tiba,* 1933, V. 11, P. 907–17; 1934, V. 12, P. 27–33.

An explanation of the principle of the electrometric and colorimetric detn. of pH, with a brief outline of its applications in the dyeing industry. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2539.) (W)

Piece-Bleaching Machinery. A. Grunert. *J. Soc. Dyers & Col.,* 1933, V. 49, P. 285–90.

An account of modern app. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2910.) (W)

Polyvinyl Compounds and Their Application in the Sizing of Rayons. M. Jeanny. *Russa,* 1933, V. 8, P. 1017–21; 1934, V. 9, P. 11–15.

A review of recent literature and pats. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2540.) (W)

PRODUCTION OF HILIOINDOSCARLET S ON THE FIBRE. Morand Baumann. *Bull. soc. ind. Mulhouse,* 1933, V. 99, P. 636. (Sealed note of 1910.) Report. Battegay. *Ibid.,* P. 363–7; *Chem. Abs.,* 1934, V. 28, P. 2187. (W)

RAW SILK: PROGRESS IN STANDARD TESTS FOR. *Am. Silk and Rayon Jnl.,* June, 1934, P. 35–7.

The article covers the uniformity tests which are essential, more data required, achievements already obtained in hosiery grading, the determination of firsts and seconds, and a discussion in brief is given of the present breadth of adoption of the nine-meter test which, according to reports, is already being used more generally than the seriplane test when it was first introduced. (S)

SULFONATED OILS: DETERMINATION OF INORGANIC SALTS IN. Ralph Hart. *Am. Silk and Rayon J.,* July, 1934, P. 41–2.

This is an abstract of report No. 3 of the Sub-Committee on Sulphonated Oils, of the American Association of Textile Chemists and Colorists. (S)

SULFONATED OILS: THE DETERMINATION OF ORGANICALLY COMBINED SULFURIC ANHYDRIDE IN. II. Ralph Hart. *Rayon and Mell. Tex. Mo.,* June, 1934, P. 53–4.

This is the second of two reports, the first of which was concerned with a method for testing the amount of water in sulphonated oils. The present report is concerned with various methods for determining organically combined sulfuric anhydride and two proposed methods are outlined in some detail. (S)

SULFUR DYES: COLORIMETRIC DETERMINATION OF. G. E. Levant and R. I. Nemtzova. *J. Applied Chem.* (U. S. S. R.), 1933, V. 6, P. 546–51.

The dye to be tested and a standard are oxidized with H_2O_2 and compared in a colorimeter. (Copied complete from *Chem. Abs.,* 1934, V. 28, P. 2909.) (W)

TEXTILE FINISHES RESEARCH. H. P. Stevens and R. Gaunt. *Bull. Rubber Growers' Assoc.,* 1933, V. 15, P. 653–66.

The object of the investigation was to find a means of utilizing latex or rubber dispersions in sizes for calico printing, dyeing and stiffening. Addn. of latex to starch-clay-olein sizes made the finish less easily removed by washing. The technic used by Hauser and Hünemörder in studying the penetration of threads by latex (cf. *Chem. Abs.,* V. 27, P. 2600, 6015) was unsatisfactory, and a new better method is to soak thread in latex, dry, stain with boiling satd. alc. Sudan III, dry, embed in a paraffin wax-stearic acid mixt., cut and mount in glycerol jelly. Without a wetting agent, there was almost no penetration, but with all com. wetting agents tested, there was complete impregnation of the threads (not of each fibre).

Neither preliminary swelling of the fibres nor surface xanthation aided penetration. C_6H_6 solns. of rubber penetrated the threads but not into the fibres. Treatment with latex of cloth for showerproofing gave insufficient protection for practical utility, except with a coating made from chlorinated rubber in C_6H_6. Data show the water absorption of cloth treated with latex. Various types of substances were ineffective in overcoming the tackiness of latex-treated cloth, as was preliminary dialysis of the latex, but prolonged immersion in hot water was successful, though the product had an increased capacity for water absorption. There is preferential absorption by cloth of the serum, *i.e.*, of the components, so that the dried product contains a disproportionately high quantity of non-rubber substances, which in turn probably account for the tackiness. This may be prevented by squeezing wet. Dyeing expts. led to uncertain results. Addn. of vulcanizing agents to the latex before impregnation and heating of the impregnated fabric overcame tackiness by the formation of a vulcanizing impregnation. Expts. aimed at the use of latex in a variety of com. products are described briefly, *e.g.*, the impregnation of stockinette with latex, in which case the product has phys. properties of promise for bandages, etc. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 2568.) (W)

WASTE FROM DYEING AND PRINTING: TREATMENT OF. Foster Dee Snell. *Rayon and Mell. Tex. Mo.*, June, 1934, P. 60–1.

A paper presented before the Division of Water, Sewage, and Sanitation Chemistry at the 87th meeting of the American Chemical Society, St. Petersburg, Fla., March 25–30, 1934. The plant under discussion does piece-dyeing and printing on silk, silk-and-cotton, silk-and-wool, rayon, and cotton materials. The colors used are principally basic and direct dyes. The plant boils off its own silk, using soap for the purpose, and bleaches with hydrogen peroxide stabilized with sodium silicate. It also does a minor amount of mercerizing. There is no hypochlorite bleaching, no chrome-dyeing, and no silk weighting. The water supply used comes from both wells and city water and is softened. The waste from the dyeing, printing, and finishing plant is increased by some 20,000 gallons of sanitary sewage per day. A table is given showing the composition of the waste in parts per hundred thousand and some details of the chemical treatment involved is provided together with a brief statement of cost which is said to be four and six-tenths cents per thousand gallons for chemical, or $13.80 for chemicals per day. The labor cost is said to be small but dependent upon the type of sedimentation basin installed. Effluents treated as above do not show exhaustion of methylene blue within 7 days, in spite of their high values for organic solids and oxygen consumed. They are therefore sufficiently stable so that the discharge of the effluent into a stream containing fish and plant life will not be objectionable. The hardness of the stream is undesirably increased by such discharge, but this increase is said to be less objectionable than the presence of dyes and other organic waste products. (S)

WOOL: LOADING OF. L. Armand. *Tiba*, 1934, V. 12, P. 83–9.

A brief review. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3237.) (W)

IV. Research Methods and Apparatus

Nomograms for the Determination of the Combined Number of Yarns. (German.) Otto Reinhardt. *Mell. Textilber.*, May, 1934, P. 201–3.

This is an elementary discussion of the simpler types of alignment charts as applied to problems of textile manufacture. The methods of construction and something of the theory back of the use of multiple charts is given and several examples are printed to show the methods of computation of the resultant number of yarns made by combining say 40s, 30s, 24s, and 15s. (S)

Photometer of Special Application to Routine Textile Measurements. R. E. V. Hampson and H. W. Richards. *J. T. I.*, March, 1934, P. T106–T121.

A description in some critical detail of a photometer in which attempt is made to measure the diffusely reflected light under conditions much more comparable with those of direct vision than are possible in the cube photometer. At the same time it is desired to produce a strong instrument, rapid in use, independent or nearly so of personal error, with a high order of accuracy and consistency and well suited to routine measurement by relatively unskilled operators. It requires only a small area of fabric which need not be detached from the rest of the article of which it is a part. The instrument is intended for use in the British Launderer's Research Association for measuring the overall departure from white of the sample under test rather than for a complete color analysis. Comment as to A. C. Hardy's photoelectric color analyser is included in the report. The device is essentially one consisting of two photoelectric cells balanced against each other and illuminated alternately from the source of light, reflected from the standard and the sample under test respectively. The light source is an automobile head lamp bulb 12 to 14 volts 48 watts mounted horizontally and surrounded by the revolving interrupter which produces the light modulation. Photographs of the apparatus together with the drawing, diagram of its operation and the wiring diagram of the photoelectric cells, the amplifying system and the illumination circuits are included. *Note:* In connection with the previous abstract the reader is advised to see *J. T. I.*, April, 1934, P. T156 for additional data which should have been included in this article but was omitted by error. (S)

Polarizing Microscope. E. W. Melson. *Instr.*, May, 1934, P. 100.

A brief account of a new polarizing microscope placed on the market by Bausch and Lomb Optical Company. This has certain adjustments which make the instrument easier to use than the average type, and possesses a number of features of new design which are noteworthy. The instrument is of interest because of the application of polarized light to textile work in general. (S)

Rayon: Determination of Hardness of. M. Vishnyakov. *Iskusstvennoe Volokno* (*Artificial Fibre*), 1934, V. 5, No. 1, P. 32–6.

The detns. made in the app. of Shpak, Atlas and Meos (*Ibid.*, 1931, V. 2, No. 12, based on the resistance of the thread to bending) produced

reliable results. The twist method proved unsatisfactory. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3893.) (W)

REFLECTOMETER AND COLOR COMPARATOR. Richard S. Hunter. *Natl. Paint, Varnish and Lacquer Assoc. Circ.* No. 461, 1934, P. 111–28.

A simple Munsell type photometer employing a pattern mirror photometer head is described. It is shown how the app. may be used to det. brightness, color, yellowing of films and hiding power. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3601.) (W)

SPECTRAL STUDY OF SOVIET ANILINE DYES. L. A. Ventman. *Anilin. Prom.*, 1933, V. 3, P. 438–43.

The results of the spectral analysis of 21 U. S. S. R. dyes are described with a view of the projected production of light filters and colored photography. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3589.) (W)

VOLUMETRIC ANALYSIS OF VISCOSES. A. S. Shpitalnuii and R. S. Lyasch. *Iskusstvennoe Volokno* (*Artificial Fibre*), 1934, V. 5, No. 1, P. 40–3.

A discussion of the existing methods. (Copied complete from *Chem. Abs.*, 1934, V. 28, P. 3893.) (W)

Book Review

RAYON AND SYNTHETIC YARN HANDBOOK. Dr. E. W. K. Schwarz and Herbert R. Mauersberger. Rayon Publishing Co., New York, N. Y. (1934) 420 pp., $3.00.

The authors have endeavored to consolidate in one volume, and in relatively non-technical language, reliable information regarding the manufacture and processing of synthetic yarns. The result is a very complete compendium, well indexed and arranged for handy reference. For an initial attempt it is remarkably free from typographical and technical errors. Cellulose and the principal processes of manufacturing synthetic yarns and allied products are treated briefly, but sufficiently for a work of this kind. The same is true of a chapter on the economic and statistical background of the industry by Stanley B. Hunt, editor of *The Textile Organon*. Covered in much greater detail are chapters on physical and chemical properties, conversion into woven and knitted goods, dyeing, printing, dry finishing and special processes, analysis and testing. The authors have devoted a chapter to yarn numbering systems and calculations specifically applying to synthetic yarns, but have wisely refrained from cumbering their book with tables of weights and measures, temperatures, humidities, acid and alkali concentrations, etc., that can be found in numerous other reference books. Of particular value, and to be found only in this book, is a list of commercial rayon fabric constructions, and another of trademarked brand names of rayon yarns and other products. (C)